

FLUIDIZED BED UPGRADING OF WOOD
PYROLYSIS LIQUIDS AND RELATED COMPOUNDS

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Abstract

The effective hydrogen index (EHI) is a calculated indicator of the "net" hydrogen/carbon ratio of a pure or mixed heteroatom-containing feed, after debiting the feed's hydrogen content for complete conversion of heteroatoms to NH_3 , H_2S , and H_2O . Compounds with EHI's < 1 are difficult to upgrade to premium products over ZSM-5 catalyst due to rapid catalyst aging in continuous fixed bed processing. However, high conversions of such feeds (acetic acid, methyl acetate, and wood pyrolysis liquids) can be maintained in a fluidized bed system operating under methanol-to-gasoline conditions and employing frequent catalyst regeneration. Synergisms observed when coprocessing blends of low and high EHI model compounds also exist for a wood pyrolysis liquid. Thus, when coprocessed with sufficient methanol, the conversion and hydrocarbon yield from wood pyrolysis liquid increased by 19 and 64%, respectively, while coke yield decreased by 40%. A possible processing scheme is described in which the char penalty associated with wood pyrolysis is diminished by gasifying the carbonaceous residue and producing methanol as a cofeed for the synergistic upgrading of the pyrolysis liquids over ZSM-5.

Introduction

Zeolite ZSM-5 is particularly effective for the conversion of methanol to gasoline range hydrocarbons (1). In addition to methanol, other oxygenate feeds, including complex mixtures, can be converted as well (see, for example, references 2-7).

The effective hydrogen index is defined as:

$$(H/C)_{\text{effective}} \text{ or EHI} = \frac{H-2O-3N-2S}{C}$$

where H, C, O, N, and S are atoms per unit weight of sample of hydrogen, carbon, oxygen, nitrogen and sulfur, respectively. Model oxygenate compounds having EHI's <1 produce a poor product slate and cause rapid zeolite catalyst aging in continuous fixed bed MTG processing (3,8) using ZSM-5. Thus, after 2 hours on stream, acetic acid conversion declines from estimated high initial values to <30%. Hydrocarbons account for <10 wt.% of the products from the aged catalyst and, of the hydrocarbon portion, >70% is C₄⁻ (overwhelmingly butenes) and <25% C₅⁺ gasoline.

Cellulosic biomass is a potential source of liquid hydrocarbon fuels. Wood pyrolysis yields carbon-containing liquid products but suffers from two disadvantages. First, a large percentage of the original wood carbon is lost to a low value char by-product. Second, like the model oxygenates described above, the EHI of the liquid products is substantially less than 1.0.

The present study was undertaken to examine the potential of short contact time regenerative fluid bed processing to obviate the problems associated in extended non-regenerative fixed bed operation with such low EHI feeds.

In addition, Chang, Lang, and Silvestri (8) disclosed that reductions in zeolite catalyst aging rate and synergistic yield benefits could be realized in fixed bed operation if the low EHI (<1) feed were co-processed with a sufficient amount of high EHI (>1) constituent. In fixed bed studies, Chantal et al (9) coprocessed up to 10% methanol with an oil derived from supercritical extraction of wood chips. Although some benefits from methanol were evident, the amounts of methanol used were less than those recommended by Chang et al (8), and run durations did not exceed one hour. Consequently, it was not clear if the amount of methanol was sufficient to maximize product yield benefits and to maintain the catalyst's performance in extended continuous processing. It was of interest to us, therefore, to further examine the potential benefits of methanol co-processing for both model compound feeds and wood pyrolysis liquids in short contact time regenerative fluid bed processing.

Experimental

a) Catalyst

The catalyst used was HZSM-5 in a $\text{SiO}_2/\text{Al}_2\text{O}_3$ binder.

b) Production of Wood Pyrolysis Liquids

Sawdust (primarily pine and fir) pyrolysis was carried out at atmospheric pressure and $\sim 520^\circ\text{C}$ in flowing He. The wood charge had the following elemental analysis (dry basis):

C - 49.20%, H - 6.80%, O - 43.40%, ash - 0.60%.

c) Reactor and Run Procedures

All model compound and wood pyrolysis liquid upgrading runs were performed in a computer controlled fluidized bed apparatus (10) (Figure 1) operating cyclically to effect successive and repeated reaction/regeneration intervals. Approximately 35 cc of catalyst was charged to the vycor reactor along with 15 cc of meshed vycor. He fluidizing gas enters through a frit at the base of the tapered section of the reactor bottom. A small flow of He also sweeps through the feed oil sidearm inlet line. The total He flow (850 cc/min.) plus the vapor phase reactant and products maintain the bed in vigorous motion which, in turn, insures good temperature control. Runs were carried out at 1 WHSV based on the low EHI feed component, 410°C and atmospheric pressure. The catalyst was automatically oxidatively regenerated after each 10-20 min. reaction interval.

The product water phase was separated and gc analyzed for oxygenates from which conversion could be calculated. The hydrocarbon product layer contained only a very small amount of oxygen (<1%). Liquid hydrocarbon product was also subjected to gc analysis as were gaseous products, the latter being checked for their hydrocarbon and CO_x contents. Coke was calculated by the computer from on line CO and CO_2 IR data collected during each catalyst regeneration. Elemental and total material balances were generally >95%. Results presented were normalized to a no loss basis.

Results and Discussion

A) Model Compound Conversions

Experimental data are presented in Table 1. Two conversions are presented for each run. "Total conversion" represents the conversion to all products, while "conversion to non-oxygenates" represents conversion to all hydrocarbon, CO_x and H_2O products. The overall yields from the methanol experiment ($\text{EHI} = 2.0$) are in reasonable agreement with data obtained in the fluid bed MTG process (11). The hydrocarbon gas products, however, are higher in propene and lower in isobutane, probably due to the lower reaction pressure used in this study.

A-1) Conversion of Acetic Acid and Methylacetate

The data obtained for acetic acid illustrate several interesting points which can be contrasted with the fixed bed operation cited above. First, total conversions >90% may be maintained indefinitely provided periodic catalyst regeneration is employed. In spite of its having an EHI of 0, which assumes that oxygen is rejected as water, our experimental data show that decarboxylation takes place to a large extent. As a result, by rejecting oxygen as CO_x , substantial production of hydrocarbons is possible. Hydrocarbon liquid product yield is ~80% larger than that obtained at 2 hours processing time in the non-regenerative fixed bed operation (18.3% vs <10%) and ~65% of the hydrocarbon product is C_5^+ gasoline with a predominantly aromatic character. This high selectivity toward aromatics formation is consistent with the low effective hydrogen content of the "hydrocarbon" fraction of acetic acid.

On a weight basis, acetic acid yields only 40% as much hydrocarbon as methanol. The lower yield is primarily due to decarboxylation, and to a small extent, to coke and CO production.

Methyl acetate has an EHI of 0.67 and thus, ordinarily, would also be considered difficult to process. Its net hydrogen content, however, is substantially higher than acetic acid's. Because of its higher carbon content (48.6% C) and despite decarboxylation and coking reactions, the observed hydrocarbon yield remains comparable to that of methanol. Moreover, hydrocarbon selectivity for direct conversion to C_5^+ gasoline is higher than acetic acid or methanol (79.5%). Thus, the direct yield of C_5^+ gasoline is 32.1% on charge vs 23.3% for methanol.

From a hydrogen balance standpoint, both acetic acid and methyl acetate reject less H_2O and more CO_x than methanol, with resultant C_5^+ liquids having effective H/C's of ~1.3 vs ~1.7-2 for methanol processing.

A-2) Conversion of Mixtures of Acetic Acid and Methanol

Processing a 1.9/1 or a 3.8/1 molar mixture of CH_3OH and acetic acid provided observations similar to those already disclosed by Chang, Lang and Silvestri (7), viz, an enhancement in C_5^+ liquid yield at the expense of C_4^- vs what might be expected if the mixture behaved as the average of its two components, the calculated values for which are shown in parentheses in Table 1. The selectivities of the hydrocarbon products amplify the observed synergism with respect to C_5^+ liquids. Furthermore, there is an enhancement in total hydrocarbon yield vs linear combination expectations.

The means by which this is accomplished is illustrated in Figure 2, which shows the effect of increasing mole percent methanol in the MeOH /acetic acid charge and attendant decrease in

oxygen rejection as CO_2 and increase in oxygen removal as H_2O . Thus, more carbon remains available to form hydrocarbon products, much of it becoming C_5^+ liquids.

The above findings demonstrate that short contact time fluid bed reactor operating in a cyclic mode can be used to process low EHI compounds to yield substantial amounts of C_5^+ liquid hydrocarbon products.

By co-processing a low EHI material with a high EHI compound such as methanol, a shift in oxygen rejection from decarboxylation to dehydration takes place. The shift results in an increased yield of hydrocarbons.

The reaction of acetic acid may have potential application in converting fermentation products to hydrocarbons. Acetic acid is a major by-product in bacterial fermentation of biomass to ethanol (12). Mixtures of acetic acid and ethanol may also be processed to hydrocarbons (13).

B) Wood Pyrolysis Liquid Upgrading

The products from sawdust pyrolysis at 520°C in flowing He at atmospheric pressure produced the yields shown in Table 2. Because the object of these experiments was to track the amount of wood carbon which could be converted to hydrocarbons by pyrolysis/ZSM-5 upgrading schemes, the amount of water produced by pyrolysis was not measured, and water in the pyrolysis liquids was fed along with the oxygenate products in subsequent ZSM-5 processing. Elemental analyses and the apparent EHI's (including any water) are presented in Table 3. Inspection of these data indicate that the liquid products contain about 31% of the original wood carbon. The char product accounts for another 49 wt% of the original wood carbon and is available for indirect liquefaction by methanol synthesis. The remaining 20% of the wood carbon becomes CO , CO_2 and methane, about half of which (as CH_4 and CO) is also potentially available for conversion to methanol.

The two pyrolysis liquid layers were homogenized (EHI of the blend was 0.34) by high speed mixing en route to the fluid bed catalytic reactor. The oxygenate conversion obtained at 410°C and 1 LHSV was 67.9% with the product selectivity distribution shown in Table 4A.

Next, the two pyrolysis liquid layers were dissolved in methanol at a 1:1 weight ratio. The solution had an apparent EHI of ~1.3 which meets the recommendations set forth by Chang et al (8). The solution was fed to the reactor at 2 WHSV so that the WHSV based on the pyrolysis liquid feed would be identical to that employed when processing was performed without methanol. In this case, the overall conversion, including methanol, was 90.3 wt%. Under these conditions, methanol alone converts completely and produces ~56 wt% H_2O and 44 wt% hydrocarbon products (11).

Conversion of the pyrolysis liquids (after subtracting the products from methanol) therefore was 80.8 wt%. The selectivity distribution of the net converted products from the pyrolysis liquid is shown in Table 4B.

The results from methanol co-processing are summarized in Table 5. They show diminished decarboxylation, greatly enhanced hydrocarbon yields, greatly reduced coke yields, and improved overall conversion. Thus, with low EHI wood pyrolysis liquids, methanol co-processing has effects similar to those observed for model compounds. In comparison, in fixed bed processing at low methanol concentrations, Chantal (9) also observed conversion enhancements and diminished decarboxylation. Although it was suggested that the presence of methanol may lead to reduced coke yields, the data were variable with increased coke accompanying increased methanol in the feed in several instances. This was likely due to inadequate amounts of methanol co-feed as discussed above. Also, coke yields were fairly high suggesting that the amount of methanol employed would have been insufficient to sustain catalyst performance over extended operating times.

C) Potential Processing Scheme

The advantages of co-processing methanol and pyrolysis liquids are further illustrated by a comparison of two potential process arrangements shown in Figures 3 and 4. A major feature common to both is the use of the pyrolysis char as a cheap source of methanol.

Figure 3 shows the products obtained in a scheme in which direct upgrading of the wood pyrolysis liquids over ZSM-5 occurs in parallel with upgrading of methanol obtained from synthesis gas derived from gasification of the pyrolysis char. In Figure 4, the methanol is mixed with the pyrolysis liquids prior to co-processing over ZSM-5. Approximately 40 lbs. of methanol is potentially available from the char and pyrolysis gas products. This amount would provide a weight ratio of methanol/pyrolysis liquids of 0.73. Since the EHI for this mixture (~1.2) exceeds 1 and is quite similar to that of the 1/1 mixture described above, comparable product distributions should result.

In the parallel processing scheme, a total of 20.6 lbs. of hydrocarbon (~85% C₅⁺ gasoline, including alkylate) per 100 lbs. of total feed (pyrolysis liquid and methanol) is obtained. In the co-processing mode, ~3 lbs. of additional hydrocarbon result concomitant with reduced oxygenates and coke.

Stated differently, without char gasification recycle of pyrolysis liquid oxygenates to extinction over ZSM-5 yields <10% of the original wood carbon as hydrocarbon products. Parallel upgrading of methanol derived from char gasification can increase this value to ~36%, while methanol co-processing boosts the percent of wood carbon transformed into hydrocarbon products to ~42%.

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TABLE 1

410°C, 1 atm., 1.0-1.1 WHSV, 20 min. reaction intervals
HZSM-5 in SiO₂/Al₂O₃

	Methanol CH ₃ OH	Acetic Acid CH ₃ COOH	Methyl Acetate CH ₃ CO ₂ CH ₃	1.9/1 (molar) MeOH/ Acetic Acid	3.8/1 (molar) MeOH/ Acetic Acid
EMI of Charge	2.0	0.0	0.67	1.0 (1.0)	1.3
Total Conversion	98.6	91.2	89.4	>91 (94.9)	95
Conversion to Non-Oxygenates	98.6	79.8	86.1	90.4 (89.2)	--
<u>Products (Wt.% of Charge)</u>					
CO	0.0	3.7	6.2	2.1 (1.8)	1.1 (1.2)
CO ₂	0.2	31.4	17.6	9.4 (15.8)	5.2 (10.6)
H ₂ O	55.8	28.4	21.5	45.3 (42.1)	48.8 (46.7)
Oxygenates	1.4	20.2	13.9	9.6 (10.8)	5.2 (7.7)
C ₁ Hydro- carbon gas	19.0	3.8	6.0	7.9 (11.4)	9.9 (13.9)
C ₂ Liquid Hydrocarbon	23.3	10.6	32.1	24.9 (17.0)	28.7 (19.1)
Total Hydro- carbons	42.3	14.4	38.1	32.8 (28.4)	38.6 (33.0)
Coke	0.3	1.9	2.7	0.8 (1.1)	1.1 (0.8)
<u>Wt. %'s of Hydrocarbon</u>					
C ₁ + C ₂	5.4	1.5	5.6	7.2	7.6
C ₃ ^o	1.6	0.1	0.7	0.4	0.6
C ₃ ^a	25.9	5.2	6.7	13.8	14.2
iC ₄ ^o	5.5	0.5	0.3	0.4	0.5
nC ₄ ^o	0.4	0.3	0.0	0.1	0.1
C ₄ ^a	5.8	15.7	1.4	1.6	1.9
Total C ₄ ⁻	44.6	23.3	14.7	23.5 (34.0)	24.9 (37.5)
C ₅ ⁺ (gasoline)	54.7	65.0	78.7	74.1 (59.8)	72.3 (58.1)
Coke	0.7	11.7	6.6	2.4 (6.2)	2.8 (4.4)
H/C (effective)* of C ₅	1.7	1.3	1.3	~1.4	~1.4

*Small amounts of oxygen were observed in the C₅⁺ liquid. The use of the effective hydrogen index corrects for this.

Table 2
Wood Pyrolysis at 520°C and 1 atm.

<u>Product</u>	<u>Wt. %</u>
CH ₄	1.4
CO	7.1
CO ₂	8.5
Liquid Oxygenates	55.0
Char	28.0

Table 3
Elemental Analysis, wt%

	<u>Sawdust</u>	<u>Liquid Layer 1 (51%)</u>	<u>Liquid Layer 2 (4%)</u>	<u>Char</u>
C	49.2	25.9	55.0	87.3
H	6.8	8.8	7.5	3.9
O	43.4	65.3	37.5	8.0
Ash	0.6	-	-	No Data
EHI	0.3	0.3	0.6	-

Table 4A
Product Distribution from Conversion
of Wood Pyrolysis Liquids

	wt. %
	——
CO	0.7
CO ₂	10.5
Water	70.7
C ₁ -C ₄	2.5
C ₅ + Hydrocarbons	6.0
Coke	9.6

Table 4B
Product Distribution from Conversion of Pyrolysis
Liquid When Processed in Conjunction with Methanol

	Wt. %
	——
CO	-
CO ₂	-
Water	82.1
C ₁ -C ₄	2.7
C ₅ + Hydrocarbons	11.2
Coke	4.0

Table 5
Advantages Resulting from Methanol Co-Processing

	Pyrolysis Liquids	Pyrolysis Liquids + Methanol (1:1 wt/wt)	% Change
Net Conversion, wt. %	67.9	80.6	+18.7
Hydrocarbons, wt. %	8.5	13.9	+63.5
Coke, wt. %	9.6	4.0	-41.7

FIGURE 1: CYCLIC FIXED FLUID BED APPARATUS

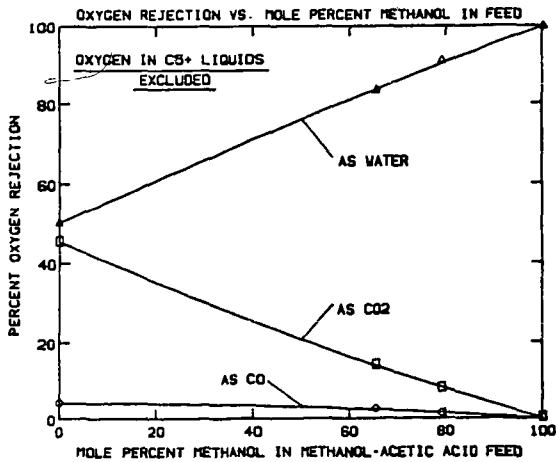
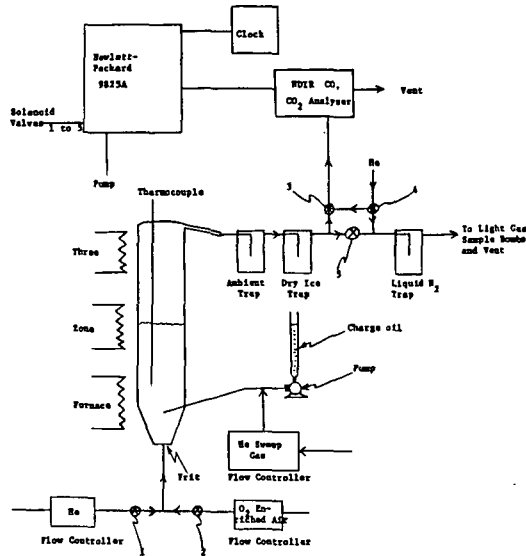


FIGURE 2

FIGURE 3

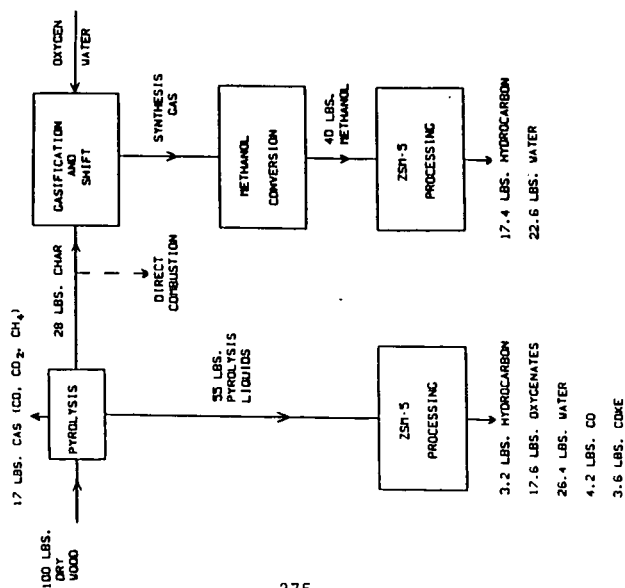
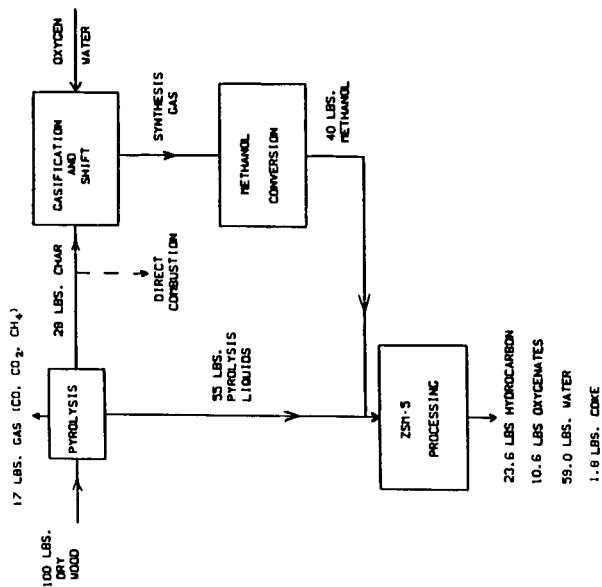


FIGURE 4



CONVERSION OF VACUUM PYROLYTIC OILS FROM POPULUS DELTOIDES OVER H-ZSM-5

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INTRODUCTION

As biomaterials are structurally and chemically complex, biomass thermochemical conversion processes^(1,2) produce complex fractions including a liquid fraction which, depending on the process, can be obtained in large (liquefaction, pyrolysis) or small yields (gasification). These liquids have found little utility because of their large contents in oxygen which implies low heat values, instability and corrosive properties. Two routes have been tested^(3,4) in order to produce hydrocarbons from these liquids. The first one involves hydrotreatment with either H₂ or H₂ + CO over classical hydrotreatment catalysts. The second route is the simultaneous dehydration and decarboxylation over HZSM-5 zeolite catalyst in the absence of any reducing gas.

Soltes and Lin⁽⁵⁾ achieved significant deoxygenation of various biomass tars from gasification/pyrolysis processes, in the presence of hydrogen-donor solvents (cyclohexane, tetralin, decalin) and various silica-alumina supported metals catalysts. Elliot and Baker⁽⁶⁾ performed hydrodeoxygenation of the products of a process of liquefaction in the presence of CO at high pressure, using NiS, CoS and MoS₂ catalysts. Hydrodeoxygenation of a biomass tar can be achieved when phenolic compounds are in high concentrations. In wood pyrolysis however, the liquid products contain large amounts of low molecular weight organic acids, ketones, aldehydes and furans as well as phenolic compounds in the methoxy- or dimethoxy⁽⁶⁻⁸⁾ substituted forms. These mixtures are thermally instable in typical hydrotreating conditions.

The second route however seems more appropriate for the conversion of pyrolytic oils. It was indeed shown that a large variety of oxygenated compounds can be converted into hydrocarbons over H-ZSM-5⁽⁹⁻²⁰⁾. In all cases hydrocarbons in the gasoline range are obtained due to the shape selective properties of this zeolite catalyst⁽²¹⁾. Moreover a remarkable resistance to coking is observed due to the sterically restricted transition state selectivity effects, and these properties are also of considerable interest in the context of pyrolytic oils upgrading. Works along this line have been performed by Chantal et al.^(22,25) working with oils derived from Aspen Poplar by dense gas extraction, Frankiewicz⁽²³⁾ who used a dual process combining pyrolysis of solid wastes with a catalytic converter and Mathews et al⁽²⁴⁾ who treated small fractions of the oils produced from wood by their thermochemical process.

In the present paper we report a study of the conversion over H-ZSM-5 catalysts, of the fractionated oil produced by vacuum pyrolysis of *Populus Deltoides* wood in a process demonstration unit⁽²⁶⁾.

EXPERIMENTAL

Pyrolytic oil

The oil under study was produced by the vacuum pyrolysis process, currently under development at LAVAL University and CRIQ⁽²⁶⁾. The PDU is a six-hearth furnace, 2m high and 0.7 m in diameter. In this unit, the organic vapours and gaseous products are rapidly removed from the reactor through a series of outlet manifolds. Then the

vapours are condensed in a primary cooling unit, and recovered as a liquid fraction for each hearth. As shown in Figure 1 four additional liquid fractions are collected in the secondary cooling unit. In this work only the fractions from the primary cooling unit have been studied and designated as oils #1 to #6 corresponding to the six hearthes from top to bottom.

In standard pyrolysis experiments using *Populus Deltoides* chips, the pressure in the reactor was lower than 80 Torr and the hearth temperatures were 215, 275, 325, 370, 415 and 465°C from top to bottom respectively. Table 1 gives some analytical results for these six oils. The low water contents are due to the separation effect of the primary cooling unit. Formic and acetic acids are considered the most abundant single organic compounds in these oils.

Conversion Reactor

The experimental set-up is a slightly modified version of a reactor described previously⁽²²⁾. As heating the pyrolytic oils to the reaction temperature is believed to induce thermal polymerisation/condensation reactions, a device was designed in order to preheat the vaporized feed and condense at an appropriate temperature the heavier products. This device is described in Figure 2. Using a syringe pump (SAGE 220) the liquid oil is injected in a controlled flow of helium (≈ 6.0 SCC/min) and first fed to an empty pyrex tube maintained at the same temperature than the tubular reactor. At the outlet of this tube the gas passes through a hot trap (150°C) where a heavy fraction is condensed. The gas flow then enters the microcatalytic pyrex tubular reactor and it is led to the heated (200°C) automatic sampling valve of a Gas Chromatograph (Perkin Elmer, Sigma 115) through a heated line (160°C). After the valve the products are collected as three fractions in three successive traps maintained at 4, -76 and -196°C respectively.

After a test the tubular reactors can be transported to another set-up where they can be regenerated in a controlled flow of dry air at 500°C. The CO₂ and H₂O produced are adsorbed over ascarite and drierite respectively and weighed. The sum of the masses of carbon in CO₂ and hydrogen in H₂O was determined and compared to the measured mass of the coke deposited in each of the two pyrex tubes.

Each experiment was performed using 1.0 ± 0.2 g of one of the three catalysts designated as H-22, H120 and H-450 undiluted. These are the H forms of ZSM-5 samples prepared by the procedure described as method B' by GABELICA et al⁽²⁸⁾. They have Si/Al ratios of 22, 119 and 452, and sodium contents less than 220 ppm as determined by PIXE⁽²⁹⁾.

The GC on line with the reactor was equipped with TC and FID detectors and a Porapak-Q column (6 ft, 1/8" OD, 80-100 mesh). In instances where peak identification was in doubt, the fraction in the 4°C trap was further analyzed using another GC (Perkin Elmer Sigma 3) equipped with a FID detector and a capillary column DB-1 (30 m).

In typical runs, oil was injected for about 3 000 s but chromatographic analysis was started at 2 000 s for all experiments.

Experimental design

A statistical experimental design was employed to study the effect of the process parameters, namely, temperature (350-450°C), space velocity CLHSV = 0.5-2.5 h⁻¹) and oil fraction, on various response variables. In order to reduce the number of experiments, a Box-Behnken experimental design⁽³⁰⁾ was selected. This design is visualized as a cube in Figure 3. Since 6 oil fractions were studied two Box-Behnken cubes were used in order to minimize the number of experiments by studying three oils

at a time. Even though a discrete variable is employed to represent the oil, in reality the hearth number (1 to 6) follows the reaction temperature on the hearth which is continuous. The experiments were performed in a random manner.

RESULTS AND DISCUSSION

Table 2 shows the experimental results and conditions for the catalytic upgrading tests of the six pyrolytic oils. It gives the weight percents of the various fractions of products collected. Coke #1 corresponds for example to the total weight of the material deposited on the wall of the empty pyrex tube whereas coke #2 is the one left in the tubular reactor (on the catalyst) at the end of a test. The tar collected in the hot trap is designated as the residuum, whereas the cumulative mass recovered in all three cold traps is indicated as "traps".

The composition of the "traps" fraction is the one of the stream leaving the reactor. It is given in Table 2 in a condensed manner as weight percents of various components including C₅-C₁₀ hydrocarbons, C₁₀⁺ hydrocarbons and oxygenates. These oxygenates are mostly comprising phenolic and furanic compounds. Figure 4 shows some of the characteristics of the six pyrolytic oils. The average molecular weight varies in a continuous manner with the hearth number, showing a maximum value for the oil produced on the 3rd hearth and a minimum value for the one from hearth No 6.

It must be noted that the sum of weight fractions of acetic and formic acids is following a similar pattern except for the oil No 5 which contains much formic acid and is therefore much more acidic. The low content in formic acid of oil No 6 is a clear indication that the solid residue leaving hearth No 5 is very different in nature from the one from hearth No 4 bearing much less intact or slightly degraded cellulose (the main source of formic acid) and much more recondensed material. Figure 5 shows for each oil the average values of the weight percents of coke #1, residuum and the yield in C₅-C₁₀ hydrocarbons. It is interesting to note that at least for the first four oils these values are obviously correlated with both oil average molecular weight and acidity (Figure 4). As expected, coke #1 is higher when the oil is heavier, but the residuum is much smaller. This last result can only be understood if the residuum is seen as an intermediate product of gas phase depolymerization which would be faster for the most acidic mixtures. Indeed for example the low residuum value obtained with oil No 5 would then be the result of this oil being much more acidic than the others.

The C₅-C₁₀ yield is also correlated with \bar{M}_w (up to oil No 5) but this correlation is the result of a more intricate interaction of various factors. C₅-C₁₀ yield does not depend only on molecular size or acidity of the oil but also on its chemical nature. Oil No 3 which contains more lignin fragments is liable to yield small phenolics which are volatile enough to reach the catalysts but which are not converted to hydrocarbons. Similarly oil No 6 which is believed to contain less polysaccharides pyrolysis products shows a very low C₅-C₁₀ yield.

The effect of the various parameters on the "traps" weight percent is reported in Figure 6. This term represents roughly the fraction of the oil reaching the catalyst and must therefore be considered as a yield for the preliminary thermal processing. The curves are drawn not taking into account the results for oil No 5. Comparing the curves obtained at 350 and 450°C (both at 1.2 LHSV) shows that increasing the temperature increases the depolymerisation of the oils components. The two curves at 400°C and 0.5 and 2.5 LHSV show that increasing the residence time in the empty tube and the hot trap increases also the depolymerisation yield.

These results show the interest of the experimental procedure adopted in this work as this gas phase thermal depolymerisation which happens at the same temperature than

the catalytic process can be studied separately. This is not the case when the vaporized oil is directly injected onto the catalyst and both processes happen simultaneously.

Figure 7 gives the yield in C₅-C₁₀ obtained for the various oils as a function of temperature and LHSV. Comparing the curves at 350 and 450°C shows that a rise in temperature increases this yield in proportions roughly similar to the increase of the "traps" fraction (see Figure 6). This suggests that the most important effect of temperature is to increase the yield of thermal depolymerization. This is confirmed by the fact that the oil No 5 which is the most acidic and is more thoroughly depolymerized (yielding a higher "traps" fraction) is also showing the highest C₅-C₁₀ yield. Similar observations can be made for the effect of contact time at 400°C.

It is interesting to note that for several oils (No 1, 2, 4 and 5) yields close to 30% have been reached. This is to be compared with the results of Chantal et al⁽²²⁾ who obtained maximum yields of 15-17% from SCE oils converted on ZSM-5 in a one step process. Figure 8 shows the variations of the percents of oxygenates in the traps. In line with previous discussion, maximum oxygenates are obtained from oils No 3 and 6 which contain respectively more lignin fragments and more product of high temperature decomposition of recondensed material and which therefore both contain more phenolic compounds.

Time on stream data

Figure 9 reports the results of a set of experiments (not shown in Table 2) designed to assess the deactivation behaviour of the catalyst. In these experiments the feed was a mixture of the six oils. It was injected for a fixed time in the reactor assembly maintained at 400°C. Then the gases leaving the reactor were analyzed and the injection of oil was stopped until the chromatographic analysis was completed, at which time the injection was restarted for another fixed time and this operation was repeated three times.

Figure 9 shows that the composition of the product changes with time on stream, with deactivation appearing after 250-500 s. The decrease in deoxygenation activity is seen from the decrease in H₂O, CO, CO₂ and the increase in oxygenates. The appearance of C₁₀⁺ aromatics in the products is of special interest. Since such large compounds cannot be generated within the pores of the ZSM-5 zeolite⁽²¹⁾, they can only be generated either on the external acid sites or from the coke deposit as postulated recently⁽¹³⁾. This would also explain the evolution of the C₅-C₁₀ aromatics distribution with time on stream, showing a relative increase in C₁₀ as well as C₁₀⁺.

The time scale for catalyst deactivation is showing the great resistance of the ZSM-5 catalyst to coking. At similar temperatures for example a pellet of H-Y cracking catalyst is deactivated within 2-3 seconds in the FCC process.

CONCLUSIONS

The experimental set-up used in this work allowed to decouple the gas phase thermal conversion of the pyrolytic oils from the catalytic upgrading. These two sets of reactions happen in the same temperature range and are therefore simultaneous when the oil is directly fed to the catalyst. Preliminary thermal conversions include some coking and an important thermal depolymerization. Both reactions are accelerated in the presence of volatile acids in the gas phase. Moreover performing both reactions in a preheater is beneficial to the catalytic conversion first because the deactivation of the catalyst is less important and secondly because depolymerized fragments yield higher conversions to hydrocarbons. C₅-C₁₀ hydrocarbon yields as high as 30 wt% have been consistently obtained for reaction times of 2000 s.

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OIL #	% WATER*	FORMIC ACID WT %	ACETIC ACID WT %	\bar{M}_w ** Mean-Molecular Weight
1	7.8	2.64	3.63	342
2	5.4	2.34	4.13	528
3	4.4	3.73	5.18	572
4	3.9	4.40	3.26	393
5	7.0	7.25	3.16	233
6	3.8	2.60	2.26	123

* determined by Karl-Fisher
 ** determined by GPC

TABLE 2 Experimental Conditions and Results of Catalytic Upgrading of Pyrolytic Oils.

OIL #	TEMP. °C	LHSV h ⁻¹	COKE wt %		RESIDUUM wt %	TRAPS wt %	PRODUCT DISTRIBUTION, wt %										YIELD C ₅ - C ₁₀
			#1	#2			CO	CO ₂	H ₂ O	C ₁ -C ₄	C ₅ -C ₁₀	OXYG.	BTX	C ₇ -C ₁₀			
1	350	1.2	15.2	2.3	50.8	31.6	1.2	1.7	5.6	1.2	61.9	26.0	23.5	3.3	19.3		
1	400	0.5	21.7	6.5	10.9	60.9	0.7	0.8	3.7	2.2	48.7	25.7	21.1	18.4	29.7		
1	400	2.5	17.4	2.8	54.8	24.9	1.0	2.0	6.2	4.3	57.6	23.9	19.7	4.9	14.3		
1	450	1.2	18.7	2.3	40.9	38.1	0.9	1.1	3.2	1.4	76.8	12.0	18.0	4.6	29.3		
2	350	0.5	10.0	4.3	62.9	22.9	0.9	1.2	4.5	1.8	52.2	33.7	18.8	5.4	12.0		
2	350	2.5	30.5	3.9	31.2	34.4	1.3	2.7	5.5	1.4	51.4	29.5	13.1	8.1	17.7		
2	400	1.2	20.6	5.9	26.5	47.1	0.8	1.0	3.4	2.0	45.8	32.5	17.2	14.6	21.6		
2	400	1.2	22.9	5.1	28.8	43.2	0.9	1.2	3.8	2.5	44.4	34.1	18.8	13.1	19.2		
2	400	1.2	21.3	5.6	24.0	49.1	1.0	1.2	3.1	1.3	45.4	29.9	17.4	17.1	22.3		
2	450	0.5	30.9	3.6	9.1	56.4	0.8	1.2	3.1	2.0	48.3	36.3	18.4	8.5	27.2		
2	450	2.5	36.6	2.8	22.5	38.0	2.6	4.6	7.2	4.6	54.7	23.3	22.0	2.8	20.8		
3	350	1.2	33.1	4.3	30.7	31.9	0.6	0.7	3.2	0.6	47.0	34.0	10.7	13.9	15.0		
3	400	0.5	25.4	3.4	25.4	45.8	1.3	1.9	4.5	4.0	42.6	34.6	28.1	11.1	19.5		
3	400	2.5	19.2	3.1	46.9	30.8	0.6	0.9	2.4	1.1	34.9	48.8	8.8	11.3	10.7		
3	450	1.2	22.3	5.9	29.4	42.3	0.8	0.9	2.3	1.8	88.6	39.0	17.8	16.5	16.3		

TABLE 2

Continued ...

DIL #	TEMP °C	LHSV h ⁻¹	COKE wt %		RESIDUUM wt %	TRAPS wt %	PRODUCT DISTRIBUTION, wt %										YIELD	
			#1	#2			CO	CO ₂	H ₂ O	C ₁ -C ₄	C ₅ -C ₁₀	UNK.	BTX	C ₄ ⁺ 10	C ₅ ⁺ C ₁₀			
4	350	1.2	20.1	2.4	52.4	25.0	1.3	1.7	5.1	1.1	58.1	24.6	22.4	8.2	14.5			
4	400	0.5	23.0	2.7	32.4	41.9	1.7	2.2	6.5	2.2	52.6	25.1	27.7	9.8	22.0			
4	400	2.5	11.7	2.6	58.3	27.4	1.3	1.8	8.4	1.9	51.3	27.6	20.0	9.7	14.1			
4	450	1.2	26.3	3.5	17.5	52.6	0.9	1.3	7.1	4.2	48.0	21.9	16.7	16.5	25.2			
5	350	0.5	27.1	3.4	16.9	52.4	1.6	1.9	6.7	1.3	52.2	29.7	26.0	6.6	27.4			
5	350	2.5	21.4	8.6	28.6	41.4	0.9	0.6	8.0	1.5	54.3	31.1	22.1	3.5	22.5			
5	400	1.2	25.5	3.9	24.5	46.1	0.4	0.5	2.9	1.1	53.1	28.5	19.0	13.6	24.5			
5	400	1.2	22.1	4.1	27.9	45.9	0.6	0.9	2.1	1.2	47.9	34.3	17.2	13.0	22.0			
5	400	1.2	29.6	3.2	20.3	46.9	0.3	0.5	4.0	1.4	56.9	24.9	20.4	12.0	26.7			
5	450	0.5	30.6	5.6	9.7	54.2	0.7	0.9	2.3	3.3	52.9	36.8	22.0	2.6	28.7			
5	450	2.5	31.8	1.3	25.2	41.7	2.5	4.7	8.8	12.1	37.1	30.5	30.6	4.1	15.5			
6	350	1.2	18.7	2.9	56.7	21.6	0.2	0.3	1.7	0.2	25.1	71.0	6.9	1.5	5.4			
6	400	0.5	30.3	12.1	3.0	54.5	0.3	0.3	1.0	0.9	30.7	47.2	11.2	19.9	16.7			
6	400	2.5	10.7	2.1	68.2	19.0	1.4	1.9	7.4	2.5	30.7	21.5	19.3	11.7	10.2			
6	450	1.2	20.4	2.4	47.9	29.3	1.3	1.2	3.9	5.9	46.1	23.9	15.6	17.5	13.5			

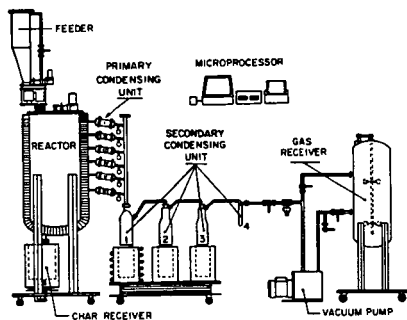


Fig. 1 - Scheme of the vacuum pyrolysis process development unit.

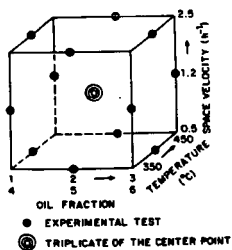


Fig. 3 - Box Behnken Experimental Design

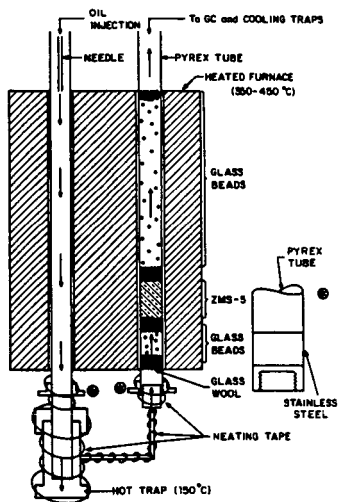


Fig. 2 - Scheme of the oil pretreatment device and reactor.

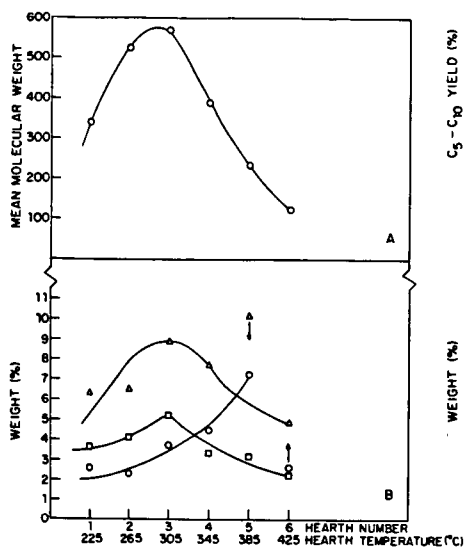


Fig. 4 - Characteristics of the pyrolytic oils. A - average molecular weight. B - Wt. % of acetic acid (□), formic acid (○) and sum of acetic + formic acids (Δ).

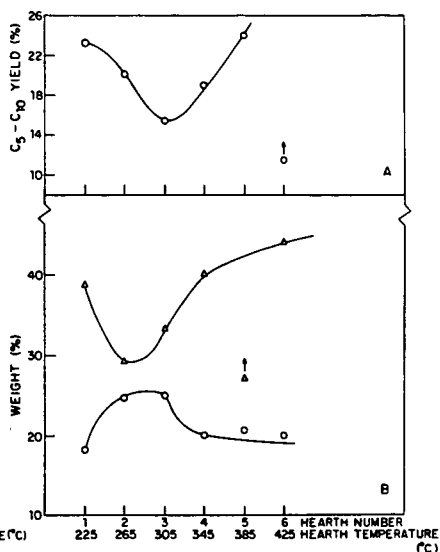


Fig. 5 - Average values for C₅-C₁₀ yields (A) and coke (B) and residuum (BA).

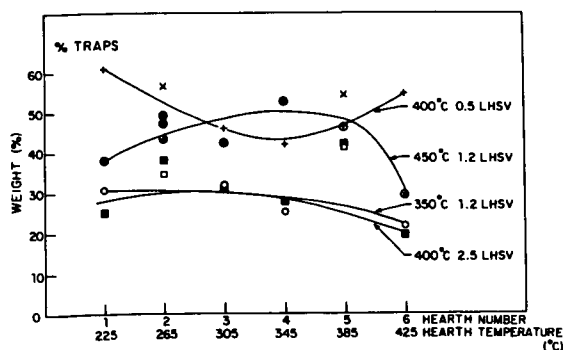


Fig. 6 - Weight % of the products collected in the traps.

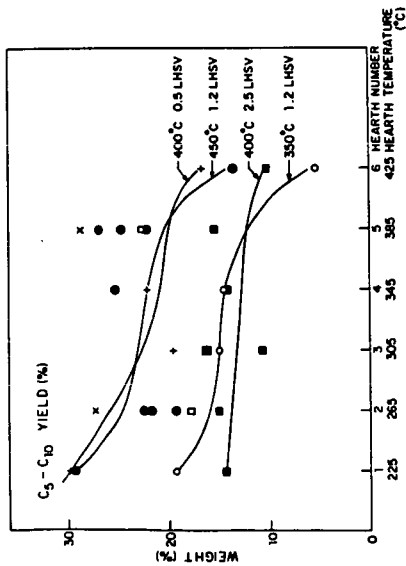


Fig. 7 - C_5-C_{10} yields

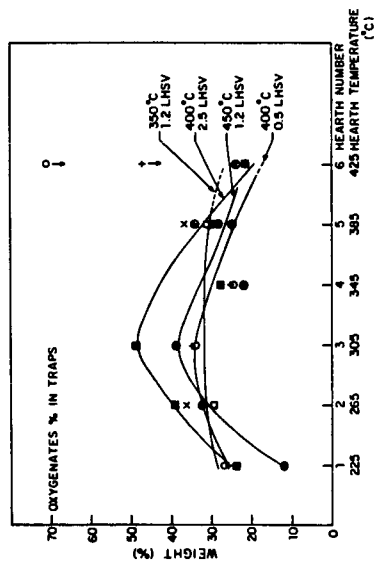


Fig. 8 - Weight % of oxygenates in the traps.

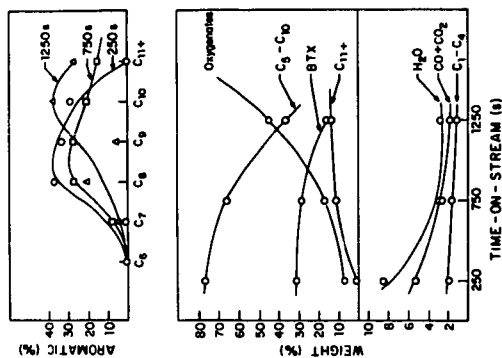


Fig. 9 - Product distribution as a function of time-on-stream

Molecular-Beam, Mass-Spectrometric Studies of Wood Vapor and Model Compounds over HZSM-5 Catalyst

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INTRODUCTION

Following research and development successes in the gasification of biomass (1), the biomass component of DOE's Biofuels and Municipal Waste Technology Division program is emphasizing direct liquefaction processes to premium hydrocarbon fuels (2). The approach being explored at SERI involves an integrated, ambient-pressure process in which primary wood pyrolysis vapor is formed by fast pyrolysis and immediately passed over a shape-selective catalyst to remove oxygen as H_2O , CO, and CO_2 . A leading vapor production method and the engineering aspects of this process are discussed by Diebold in two companion papers in this symposium (3, 4).

We report here preliminary screening results on the behavior of wood pyrolysis vapor and model compounds when passed, at high dilution, over a sample of HZSM-5 supplied by the Mobil Corporation (5).

EXPERIMENTAL

The screening is carried out using a simple, quartz, two-stage reactor coupled to a free-jet, molecular-beam, mass-spectrometer sampling system. This system and typical results for primary and secondary vapors from wood and its constituents are described in a recent publication (6). Carrier gas (He for the results shown below) is preheated in a 30 cm lower section of 2 cm ID quartz. A side arm allows introduction of solid samples to the hot gas or injection of liquids or gases through syringes. The upper 30 cm long section contains the catalyst, placed at the center of the upper section for temperature uniformity.

The catalysts used in this work are: (1) medium pore sized H-ZSM5 provided by Mobil (MCSG-2, extrudate with an unspecified amount of alumina binder); (2) medium pore sized Silicalite provided by Union Carbide (S-115, extrudate with 20% alumina); (3) large pore sized type Y Molecular Sieve provided by Union Carbide (SK-500, extrudate) and (4) silica/alumina obtained from Davidson (980-13, extrudate).

Gases and vapors emerging from the quartz reactor are immediately extracted by a sonic orifice and converted by a second orifice to a molecular beam. Expansion to molecular flow ensures rapid quenching and presents a sample to the ion source of the mass spectrometer that has not suffered wall collisions. In this way, highly condensible species can be sampled in real time. The data shown below are positive ion mass spectra using low energy (22.5 eV) electrons to minimize fragmentation.

This system has the advantage of allowing observation of the actual vapor species that enter the catalyst space and the easy observation of the breakthrough of reactant species. All product species but H_2 can be followed, but fragmentation occasionally interferes and isomers cannot be separately detected. At the moment, the technique is semi-quantitative and is viewed as a supplement to bench-scale systems with product collection for GC analysis, mass balances, and coke determinations (4).

RESULTS AND DISCUSSION

The goals of this catalyst screening project are to gain insight into the conversion of biomass pyrolysis products with a variety of catalysts and under a range of conditions. The screening results allow an assessment of several important aspects of the conversion process: the identification of promising catalysts; the determination of the critical variables in yield optimization; the effect of catalyst composition, structural properties, and physical form on product formation; the behavior of model compounds that represent the range of functionality and structure found in biomass pyrolysis vapors; the determination of relative coking rates for various catalysts and feedstocks; and the regenerability of catalysts. This experimental system was designed to study biomass pyrolysis vapors and has been used to study the fundamentals of biomass pyrolysis, both the initial condensed phase pyrolysis and the subsequent vapor phase pyrolysis (6).

This screening approach is not a stand-alone technique, however, and hence scale experimentation is needed to provide data for parameters which the screening approach does not adequately address: confirmed product identification, product mass balance, long-term studies in assessing catalyst life, and the variation of certain reactor operating conditions which have limited ranges at this scale, such as feed partial pressure or carrier gas flow rate. Initial results are reported here for the effect of the type of catalyst, the effect of weight hourly space velocity (WHSV) and temperature, the estimation of product yields, and the effect of cofeeding methanol for wood vapor conversion to organic products. The relative performance of several model compounds over H-ZSM5 has also been examined and preliminary results are presented.

The relative activities and behavior of four catalysts are shown in Figure 1 which compares the mass spectra of the products. The low-molecular-weight products (m/z 's 18-44) are under-represented in the spectra due to discrimination of the detection system against low masses in these particular experiments. Nevertheless, the uncorrected spectra are sufficient for comparing different catalysts. The H-ZSM5 zeolite was the catalyst used for most of the work in this paper. The Silicalite is also a shape selective catalyst with the ZSM-5 structure, but with nearly zero aluminum in the crystal lattice. The Silicalite gave the same type of products as H-ZSM5, but with differences in the proportions. The formation of light aromatics [benzene (m/z 78), toluene (m/z 92), xylene (m/z 106)], furans [furan (m/z 68) and methyl furan (m/z 82)], alkenes [propylene (m/z 42) and butene (m/z 56)], and naphthalenes [naphthalene (m/z 128) and methyl naphthalene (m/z 142)] are the major classes of products from wood pyrolysis product conversion over zeolite catalysts. The furans are intermediates that can be subsequently converted to other products with higher reaction severity (i.e., lower WHSV or higher temperatures). The naphthalenes are formed under higher reaction severity and are most likely undesirable products for most applications. The shape-selective nature of these two catalysts is apparent. There is no selectivity observed in the destruction of the wood pyrolysis vapors, as all pyrolysis products are destroyed. However, the higher molecular weight primary products may be converted to coke on the macrosurface of the catalyst, as will be discussed below. The Silicalite appears to be less reactive than the H-ZSM5 since fewer aromatics are formed relative to CO_2 (m/z 44) for the Silicalite, more furan is formed relative to the aromatics, more high-molecular-weight material survives (that is probably associated with the wood primary pyrolysis products), and less of the heavier alkyl naphthalenes are formed relative to the light aromatics.

The third catalyst shown in Figure 1 is a crystalline aluminosilicate derived from a wide bore, type Y molecular sieve that shows significantly less activity than the

H-ZSM5 and silicalite. The intermediate furans are comparable to the light aromatics and unreacted wood pyrolysis products (m/z 's 60, 98, 124, 150 and 164) are present in the spectrum. Olefin yields appear higher than for the first two catalysts, however.

The fourth catalyst in Figure 1 is a silica/alumina catalyst which also shows the intermediate conversion slate (i.e., furans and unreacted pyrolysis products), indicating low activity. The peaks at m/z 's 134, 148, and 162 have higher relative abundance than in the spectra from the other three catalysts and are likely due to tetra-, penta-, and hexamethylbenzene which form in higher amounts than toluene, xylene, and trimethylbenzene because of the lack of shape selectivity, which limits the product size with the zeolite catalysts.

The proportions of organic products that form from wood vapor over H-ZSM5 vary systematically with WHSV and temperature. The effects of these two parameters on the relative abundance of selected products from the conversion of pine pyrolysis products over H-ZSM5 are shown in Figure 2. The temperature was varied from 300° to 550°C and the WHSV from 0.7 to 2.0 hr⁻¹. These are compositional plots and do not directly show the yield of these components since coke will vary with these parameters and is not reflected in the product distribution. The plots of trimethylbenzene, toluene, and benzene show a trend for dealkylation with increased temperature. Trimethylbenzene decreases with temperature, while toluene increases to a maximum at 500°C and then decreases at higher temperatures. A possible explanation is that the dealkylation of trimethylbenzene and xylene lead to increased abundances of toluene, reaching a maximum at 500°C where the depletion of these heavier species and the dealkylation of toluene leads to a decrease in its relative abundance. Benzene increased throughout the temperature range studied. At higher temperatures, benzene relative abundance also increased with lower WHSV's.

The few intermediates from wood vapor are represented in Figure 2 by m/z 118 (probably benzofuran), which shows a maxima at 400°C for all three WHSV's, although the relative abundance increases with WHSV. The alkenes show a steady increase with temperature and a dependence on WHSV at the higher temperatures. The generation of alkenes under extreme reaction conditions possibly indicates that the mechanism of aromatic formation from the alkenes in methanol conversion is not followed in wood pyrolysis product conversion. The aromatics formed from wood are possibly formed more directly by the dehydration and aromatization of the primary pyrolysis products rather than from the polymerization of alkenes as in methanol conversion. The formation of condensed aromatics is also enhanced at higher temperatures, as demonstrated by naphthalene in Figure 2. The trend of lower yields of naphthalenes with lower WHSV's is surprising since these are the final products to form. The dealkylation of the naphthalenes followed the same trend as the alkylbenzenes--methyl-naphthalene went through a maximum and then decreased at higher temperatures.

In methanol conversion, the partial pressure of the feed has a major effect on the product distribution with low partial pressures leading to lower yields of aromatics since they are formed by the polymerization of the alkenes (7). The effect of increasing the partial pressure of feed on the product distribution from the conversion of biomass pyrolysis products may not be the same as with methanol since the aromatics possibly form in a different mechanism. The work reported in this paper is at low partial pressure of wood pyrolysis vapor in helium (1% by volume, assuming a vapor molecular weight of 100). Variation of this parameter remains to be studied and could provide crucial insight as to the mechanisms of both olefin and aromatic production in wood pyrolysis product conversion.

This screening technique is not the optimum method of addressing yields of hydrocarbons based on the initial weight of wood, but an experiment was performed to estimate the yield of organic products, to put the screening results in perspective. Table 1 shows estimates of the wt % of products based on the relative sensitivities of the major products in this mass spectrometric detection method. The vapors analyzed include the moisture in the feed and the water, CO, and CO₂ generated in the primary pyrolysis of the wood. Yields were estimated by correcting the composition of the vapor for coke deposition on the catalyst and the char from the initial pyrolysis. The coke was determined by weighing the catalyst before and after a known amount of wood was pyrolyzed and passed over the catalyst. The resulting estimates of the yield of organics varied from 8% to 11%, depending on the temperature and WHSV. Since the stoichiometry of wood can allow a potential yield of 30% light aromatics from wood due to the removal of oxygen as H₂O and CO (4), the 11% hydrocarbon yield represents 30% of the theoretical yield of hydrocarbons from wood. For additional stoichiometric constraints on aromatic yields, see Miebold and Scahill (4) in this symposium.

The relatively low levels of hydrogen in biomass, coupled with the high amount of oxygen to be rejected, are the reason for the 30% theoretical yield of hydrocarbons. This has led Chen et al. (8) to propose the cofeeding of methanol with carbohydrates to enrich the feedstock in hydrogen and increase the potential hydrocarbon yield. This idea was briefly explored with wood, and the product distributions are shown in Figure 3 for methanol, wood, wood-plus-methanol, and wood-plus-methanol with the methanol contribution subtracted. As in Figure 1, the peaks for water (m/z 18), CO (m/z 28 [also in part due to ethylene]) and CO₂ (m/z 44) are under-represented in these spectra due to the tuning of the mass spectrometer. The product distribution for methanol conversion at 500°C and WHSV = 2.8 (Figure 3A) shows the major classes of products: dimethyl ether (m/z's 45 and 46); the alkenes (m/z's 28 [also in part due to CO], 42, 56, 70, and 84); and the methylated benzenes (m/z's 92, 106, and 120). Alkanes are also a major product from methanol conversion but are not prominent in the runs spectra due to lower ionization sensitivity and increased ionization fragmentation. The peaks at m/z's 147 and 162 are due to penta and hexamethylbenzene, which form in high abundance when methanol is run immediately after wood, possibly due to alkylation of coke precursors and stripping from the catalyst surface. The aspen product distribution at 500°C and WHSV = 1 (Figure 3B) has similarities to the methanol, including the presence of the olefins (m/z's 28, 42, and 56) and the light aromatics. When the

Table 1. Estimated Product Yields from MBMS Data

Temp, °C WHSV, hr ⁻¹	450 2.4	450 4.2	510 2.7	500 3.6	495 4.0
Water, wt % of Vapors	63.8	50.6	45.3	49.5	50.7
CO, wt % of Vapors	10.7	19.1	23.8	19.8	18.7
CO ₂ , wt % of Vapors	14.5	18.4	16.4	17.0	15.6
Olefins, wt % of Vapors	6.9	6.3	10.3	8.8	9.7
BTX, wt % of Vapors	3.0	4.0	3.3	3.9	4.2
Sum of Organics, wt % of Vapors	11.0	11.9	14.6	13.6	15.0
Sum of Inorganics, wt % of Vapors	89.0	88.1	85.4	86.4	85.0
Yield of Organics, wt % of Wood	8.0	8.7	10.7	9.9	11.0

two are run together, the spectrum looks fairly additive with lesser amounts of olefins than in the pure methanol (Figure 3C). When the methanol contribution is subtracted from the combined run (Figure 3D), it is apparent that the yield of aromatics from the biomass components is increased due to the presence of methanol, and the distribution of products has changed with more xylene and trimethylbenzene, relative to benzene and very little alkenes. The methylation of the biomass-derived aromatics is not only increasing the yield beyond the addition of the two contributions, but is also changing the products toward higher value components. Based upon the GC analysis of the noncondensable gases (4), this increase in methylated benzenes would be expected to occur at the expense of the gaseous alkanes formed from pure methanol.

The behavior of model compounds, in a very preliminary screening, has given some insight toward potential yields. The product spectra of four model compounds are shown in Figure 4. These spectra were collected under different tuning conditions than previous results to bring up the low masses. As with Figures 1 and 2, however, these results have not been calibrated, so peak heights are not directly interpretable as yields. The best use of these model compound screening results is for product slate comparisons. The two major trends are summarized here: (1) the carbohydrate-derived ring compounds such as α -angelicalactone (Figure 4B) and furfuryl alcohol gave the greatest yields of aromatics, while lower yields were obtained from the light oxygenates, such as hydroxyacetaldehyde (Figure 4D); and (2) lignin-derived products, from catechol and guaiacol to isoeugenol (Figure 4A) and coniferyl alcohol, gave very low yields of light aromatics and total organics but were completely destroyed, indicating a high coking potential for the lignin-derived methoxyphenols and phenols.

The formation of furan from cellulose was previously reported (9). Furfural formed furan as shown in Figure 4C; methyl furfural formed mostly methyl furan with minor amounts of furan; and hydroxymethyl furan formed more furan than methyl furan.

The yield of water was always greater than the sum of CO and CO₂ for both the lignin and the carbohydrate products that were studied except for the carbohydrate ring compounds such as α -angelicalactone and furfural. Several compounds gave high yields of particular products that were more related to the functionality than the elemental composition: (1) compounds containing aldehyde groups, such as hydroxyacetaldehyde (Figure 4D) and the furfurals (Figure 4C), gave higher yields of CO (Angelicalactone also gave high yields of CO), (2) acetic acid gave a relatively high abundance of CO₂ as might be expected due to decarboxylation, (3) acetic acid and acetol gave high relative yields of alkenes relative to the heavier compounds, perhaps due to the formation of C₂ and C₃ hydrocarbons after the loss of oxygen as H₂O or CO₂, and (4) hydroxymethylfurfural gave less than half the yields of all organic products than did methyl furfural.

In addition to selected model compounds, three carbohydrates were pyrolyzed and passed over the catalyst. Levoglucosan, glucose, and sucrose gave the same distribution of product classes.

SUMMARY

The results obtained so far with wood vapor over Mobil's sample of HZSM-5 can be summarized as follows:

- Yields of total organics up to 30% of a postulated theoretical maximum yield of 30 wt % have been obtained.

- H_2O always exceeds the sum of CO and CO_2 for wood vapor products.
- Yields of olefins exceed those of aromatics, quite probably due to the low partial pressure of wood vapor in He (typically 1 vol % assuming a wood vapor average molecular weight of 100).
- Fresh catalyst is extremely active, converting all wood-derived species, even heavy lignin species, although coke is a likely major product.
- Methanol (approximately 1.5:1 methanol/wood pyrolysis vapor by weight) increased the hydrocarbon yield, mainly as xylene and trimethylbenzene.
- Product slates can be manipulated by temperature and WHSV.
- There are virtually no intermediates observed from wood vapors (as with dimethyl ether from methanol), except furan species from the carbohydrates.

It is apparent that in future work, catalyst characteristics and variations such as surface acidity, crystallite size, and Si/Al ratio should be explored. In addition, model compounds should be studied to explore the mode of oxygen removal and coking in functionalities present in wood vapor. The synergistic benefits of methanol as a hydrogen carrier should be quantified.

ACKNOWLEDGEMENTS

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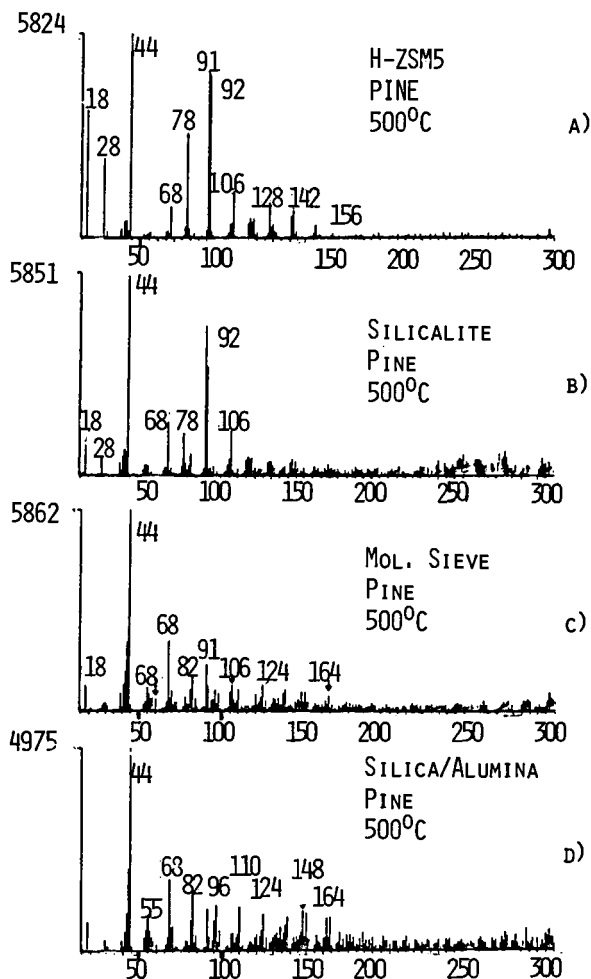


FIGURE 1. MASS SPECTRA OF THE PRODUCTS OF THE CONVERSION OF PINE WOOD PYROLYSIS VAPOR OVER VARIOUS CATALYSTS AT 500°C AND WHSV OF 1: A) MOBIL'S HZSM-5; B) UNION CARBIDE'S SILICALITE; C) UNION CARBIDE'S MOLECULAR SIEVE; AND D) DAVIDSON'S SILICA/ALUMINA.

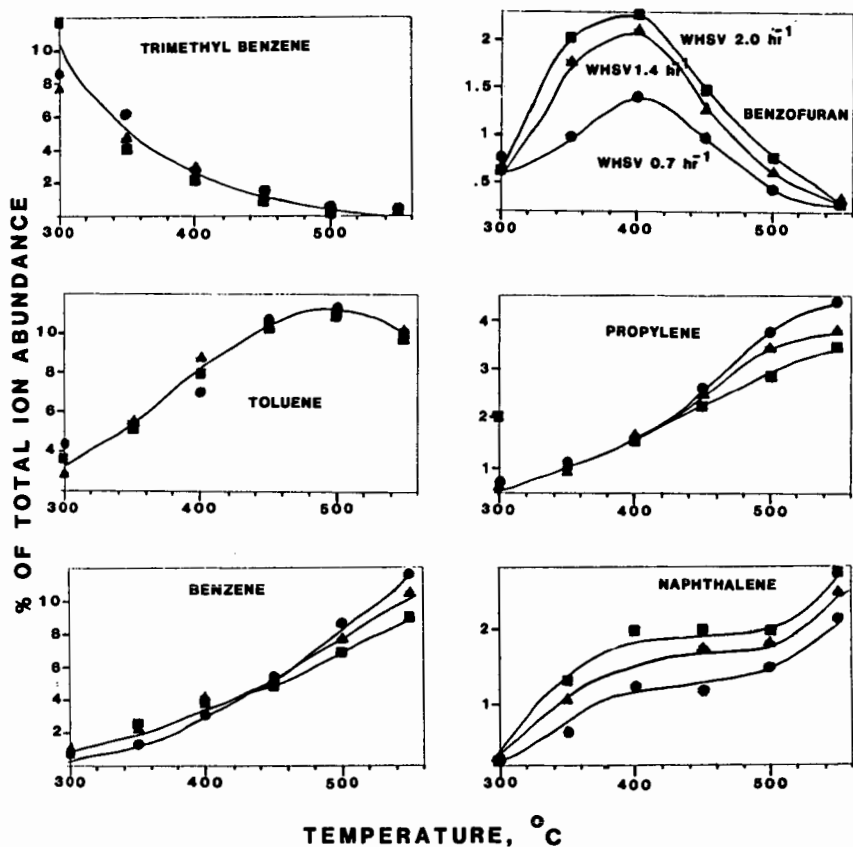


FIGURE 2. THE EFFECT OF TEMPERATURE AND WHSV ON THE DISTRIBUTION OF PRODUCTS FROM THE CONVERSION OF PINE WOOD PYROLYSIS VAPORS OVER H-ZSM5 CATALYST. NOTE: % OF ION ABUNDANCE SHOULD NOT BE EQUATED WITH % OF NEUTRAL PRODUCTS SINCE MASS SPECTROMETER TUNING AND CROSS SECTIONS FAVOR AROMATICS.

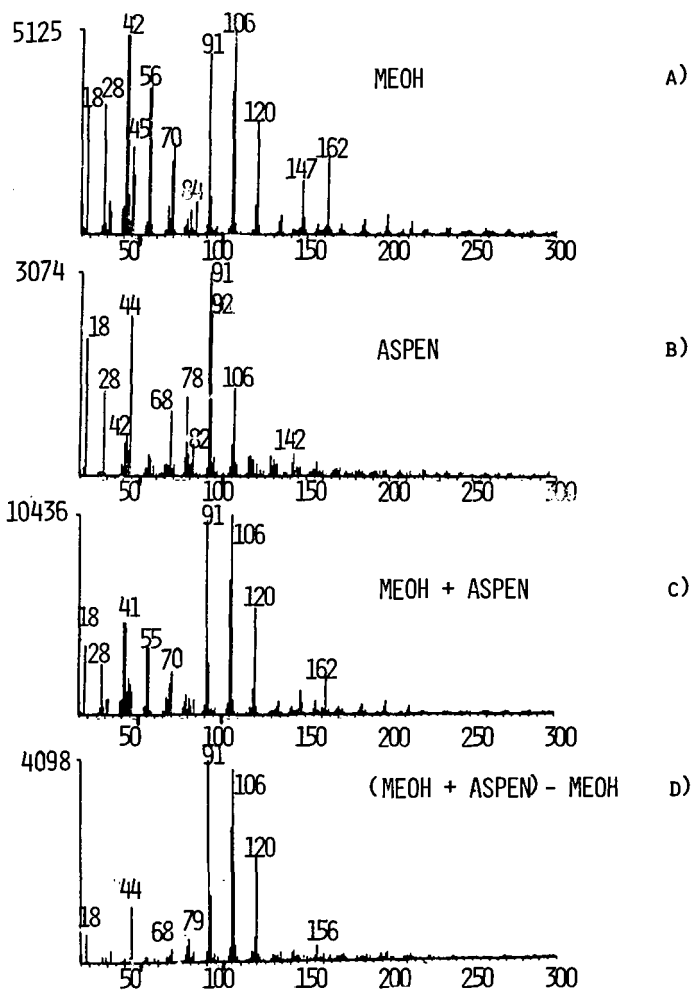


FIGURE 3. MASS SPECTRA OF THE PRODUCTS OF THE CONVERSION OF METHANOL AND ASPEN PYROLYSIS VAPORS OVER HZSM-5: A) METHANOL ALONE, 500°C, WHSV = 2.8; B) ASPEN PYROLYSIS PRODUCTS ALONE, 500°C, WHSV = 1.9; C) COFEEDING METHANOL AND WOOD USING THE CONDITIONS IN A) AND B); D) THE RESULTS IN C) WITH THE METHANOL ALONE RESULTS A) SUBTRACTED SHOWING THE ENHANCEMENT TO THE ASPEN PRODUCT DISTRIBUTION.

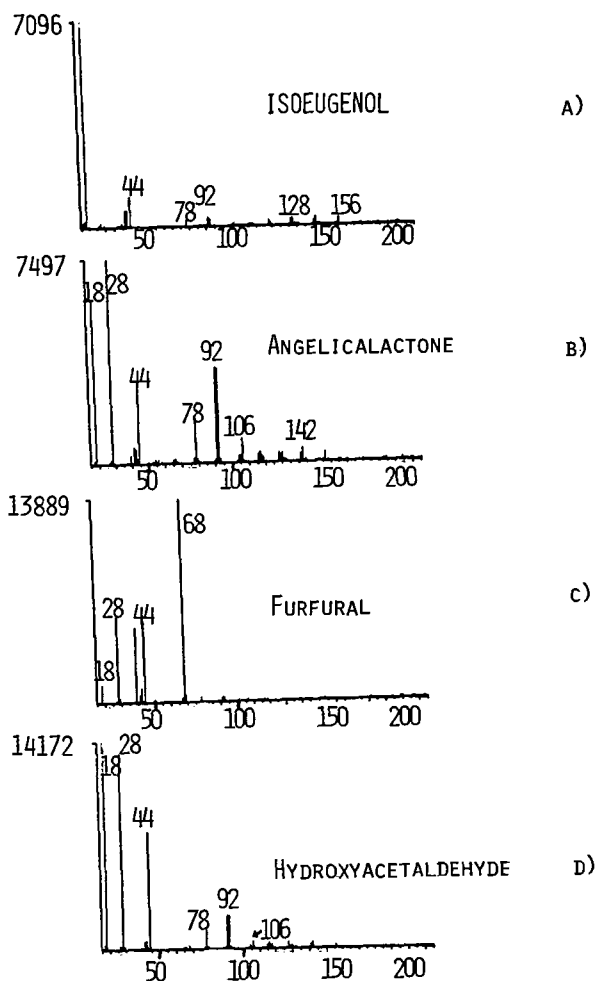


FIGURE 4. MASS SPECTRA OF THE PRODUCTS OF THE CONVERSION OF MODEL COMPOUNDS OVER HZSM-5: A) ISOEUGENOL, 500°C, WHSV = 2.4; B) α -ANGELICALACTONE, 500°C, WHSV = 2.0; C) FURFURAL, 500°C, WHSV = 1.5; AND D) HYDROXYACETALDEHYDE, 500°C, WHSV = 6.1.

**Biomass to Gasoline (BTG): Upgrading Pyrolysis Vapors
to Aromatic Gasoline with Zeolite Catalysis at Atmospheric Pressure**

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ABSTRACT

The primary pyrolysis vapors generated by the fast pyrolysis of biomass at atmospheric pressures consist initially of low-molecular-weight compounds, but which polymerize readily upon condensation. Prior to condensation, these primary vapors have been found to be very reactive with ZSM-5 catalyst to produce methyl benzenes boiling in the gasoline range. This gasoline is predicted to have very high blending octane numbers. By-products are coke, carbon oxides, water, naphthalenes, ethylene, propylene, and some phenols. The effect of different by-products on the theoretical gasoline yield is examined. Preliminary results, generated with a reactor having a fixed bed of 100 g of catalyst, are examined for the continuous feeding of never-condensed primary vapors and compared to feeding methanol in the same reactor.

INTRODUCTION

The conversion of biomass materials to high octane gasoline has been actively pursued for many years. Historically, methanol was made in very low yields by the destructive distillation of hardwoods. More recently, the manufacture of methanol has been by the reaction of synthesis gas over catalysts at high pressures. In theory, any carbon source can be used for this catalytic generation of methanol, but in practice, biomass has not been advantageous relative to coal or natural gas. Other approaches to making liquid fuel from biomass have involved the fermentation of biomass to ethanol in a rather slow process, which produces a substantial amount of by-product solids and liquid wastes. The conversion of biomass to alcohols is technically feasible, but the utilization of the alcohols as transportation fuels will require modifications to the distribution systems and to the individual automobiles. The high-pressure liquefaction of biomass to oxygenated liquids followed by high-pressure catalytic hydrogenation to form hydrocarbons is one approach to convert biomass to liquid fuels (1). However, in the last decade, Mobil has developed the use of a zeolite catalyst for the conversion of methanol to gasoline (2). This process has recently been commercialized and is now in operation in New Zealand (3). The zeolite catalyst used in the Mobil process is a medium pore zeolite, which has shape selectivity to restrict the products to methylated benzenes, isoparaffins, and olefins, while preventing the formation of coke in the catalyst pores (4). This catalyst is known as ZSM-5, and its commercial use is controlled by Mobil.

The reactivity of high-molecular-weight vegetable oils with ZSM-5 was reported in 1979 (5) and, in fact, ZSM-5 catalyst is very reactive toward most small oxygenated species to convert them to methylated benzenes and other products (6, 7). Although alcohols appear to be some of the best feedstocks for ZSM-5 catalysis due to their low coking tendencies, the petroleum industry has long made use of zeolite catalysts for the cracking of very heavy hydrocarbons to produce gasoline and about 5 to 15 weight percent coke. This suggests that the formation of coke and the need for frequent catalyst regeneration will heavily impact the reactor design, but that significant coke formation can be part of a viable commercial process. The thrust

of this paper is to examine possible stoichiometries and preliminary experimental results from using primary pyrolysis vapors made by the fast pyrolysis of sawdust at atmospheric pressure in a vortex reactor. The production of these oxygenate vapors is addressed in a companion paper (8).

STOICHIOMETRY

Although the hydrocarbon products have an unusual feedstock independence, the chemistry involved with different feedstocks over the ZSM-5 catalyst varies considerably with the functionality of the oxygen in the feedstock. As seen in Table 1, the hydroxy and methoxy groups in general have a very strong tendency to reject oxygen in the form of water, as seen for the case of methanol, dimethyl ether (9), glycerol (10), and phenols (11). Rejection of the oxygen as carbon monoxide occurs preferentially to water in a 4:1 ratio with furfural (7, 10). The reaction of n-butyl formate over ZSM-5 produces equal molar amounts of water and carbon monoxide (9). Acetic acid reacts to produce acetone, water, and carbon dioxide with only small amounts of carbon monoxide. The reaction of acetone produces largely water as the oxygen-containing by-product. The acetate group appears to decompose in such a way as to reject four times as much oxygen as carbon dioxide than as carbon monoxide, but with over 50% of the oxygen rejected in the form of water (12). Glucose and starch were reported to reject oxygen preferentially as water rather than as carbon monoxide in a 3-1/2 to 1 ratio with very little formation of carbon dioxide. Sucrose and xylose also produced very little carbon dioxide, but favored the formation of water over carbon monoxide by only 1-1/2 to 1 (7), perhaps due to the formation of some furfural as part of the intermediates. In summary, hydroxyl and methoxy groups tend to reject oxygen in the form of water; aryl ethers reject a nearly equal amount of oxygen in water and carbon monoxide; carbonyl and formate groups reject oxygen largely as carbon monoxide, and carboxyl groups reject oxygen mostly as carbon dioxide and water. With the model compounds listed in Table 1, many of these trends may also be a function of reaction conditions as well as reactants. A model compound study coupled with a process variable study is in progress at SERI with the free-jet, molecular beam/mass spectrometer (FJMBMS) (13).

The method of oxygen rejection which occurs over the catalyst has a very important impact on the potential yield of hydrocarbons, especially for a feedstock like biomass which has a relatively low hydrogen content. Although the products formed from a few compounds reacted with ZSM-5 are known for certain conditions, methods to manipulate the by-product slate are essentially unexplored. However, the desirability to reject oxygen as carbon oxides becomes quite obvious by examining potential product slates which are possible from the stoichiometry of the reacting primary pyrolysis vapors, $\text{CH}_{1.2}\text{O}_{0.49}$. Based on the assumption of a 70 wt % yield of primary vapors, Table 2 shows that of the product slates considered, the best hydrocarbon yields would be attained with oxygen rejection as carbon dioxide, and the excess hydrogen used to also reject oxygen as water. Note that the liquid hydrocarbon product assumed corresponds to xylene, C_8H_{10} , rather than to more hydrogen-rich hydrocarbons such as olefins, C_nH_{2n} (as will be discussed, the liquid hydrocarbon products actually made from these pyrolysis vapors are aromatic in nature). If carbon monoxide is the assumed carbon oxide, more carbon is needed to reject the oxygen, which decreases the potential hydrocarbon yields, as shown by reaction (2) of Table 2. If the by-product gases are a mixture of carbon oxides, methane, olefins, etc., as shown empirically in reaction (3) as $\text{CH}_{0.65}\text{O}_{0.82}$, then the gasoline yields would be lowered due to the noncondensable hydrocarbons. The formation of pure carbon could still result in considerable gasoline yields as shown by reaction (4). However, since coke formation is typically an aromatization reaction to produce polycyclic aromatic hydrocarbons containing residual hydrogen, reaction (5) is probably the more reasonable coking reaction to expect, which

produces water and coke but no gasoline at all. In summary, the more desired reactions produce carbon oxides and water as by-products. Undesired reactions produce noncondensable hydrocarbons and/or coke and water.

EXPERIMENTAL

The primary pyrolysis vapors, used as feedstock, were produced by fast pyrolysis in a vortex reactor from coarse softwood sawdust, as discussed in reference (8). After the vapors left the vortex reactor system, they were allowed to cool to the desired catalytic reaction temperature, as they passed through a tubular transfer line to the catalytic reactor. The transfer line was located inside of a series of six tubular furnaces, which allowed the vapor stream to equilibrate to the desired temperature. The residence time of the vapor in the transfer line was about one-half second prior to reaching the 2.5-cm diameter catalytic reactor shown in Figure 1. The catalytic reactor had a 30-cm-long fixed bed of 100 g of ZSM-5 containing catalyst (MCSG-2), which was located in the middle of the sixth furnace section. The catalyst was in the form of 1.4-mm diameter extrudate and supplied by Mobil Research and Development Corp. in a cooperative agreement with the Solar Energy Research Institute. The temperature of the catalyst bed was measured with an axial thermocouple inside a 6-mm thermowell. The temperature profile of the bed was determined by moving the axial thermocouple within the thermowell. A sintered stainless steel filter rated at 5 micrometers was used to remove char fines from the pyrolysis vapors. The products were collected in water-cooled condensers. The pressure in the reactor was slightly above the local atmospheric pressure at about 95 kPa. Analysis of the organic condensates was with a 5-micrometer wide bore capillary column having a length of 60 m. The capillary column was coated with one micrometer of cross-linked methyl silicones. With helium as the carrier gas, the temperature profile started at 0°C for 4 minutes, followed by a temperature ramp of 8°C/min until a temperature of 260°C was reached. Detection of the eluted organics was by flame ionization detection (FID). Identification of the major peaks was by reference materials, whereas the minor peaks were identified by a combination of the FJMBMS at SERI and a GC/MS located in the Department of Chemical and Petroleum Refining Engineering of the Colorado School of Mines. The noncondensable gases were analyzed with a Carle GC designed for refinery gas analysis, which used thermal conductivity detection (TCD) and was calibrated with a gravimetrically prepared reference mixture. Electronic grade methanol (99.9% pure) was used for comparison to the softwood feedstock.

EXPERIMENTAL RESULTS

Methanol. To verify the activity of the catalyst and to gain experience in the operation of the catalyst system, methanol was metered into a preheater tube located inside of the transfer line heated to 500°C. This preheating proved to be too severe and the products which emerged from the catalytic reactor were dominated by hydrogen and carbon monoxide in a 2:1 ratio, as shown in Table 3. This would be expected from thermal decomposition of the methanol prior to reaching the catalyst. This experiment was repeated using a preheating temperature ramp to just reach 400°C at the entrance to the catalytic reactor. The catalytic reactor was held at a nominal 400°C prior to the addition of the methanol at a space velocity (WHSV) of 0.9 g methanol per gram of catalyst. The noncondensable gas composition is shown in Table 3 and was rich in hydrogen and alkanes (methane, propane, and isobutane). The gaseous olefins would be used to alkylate the reactive isobutane to result in a highly branched-chain gasoline fraction (14). The GC for the hydrocarbon liquid is shown in Figure 2a; the liquid product contained relatively little alkanes or olefins and was dominated by methylated benzenes, such as toluene, xylenes, and trimethyl benzenes. Relatively very small amounts of naphthalenes were

seen. The temperature profile of the catalytic reactor immediately prior to and also during this experiment is shown in Figure 3. The location of the temperature-profile maxima was quite stable, which indicates that the catalyst was not significantly deactivating during the short time of the experiment. This low rate of catalyst deactivation is consistent with data published by Mobil personnel (15). The ratio of gasoline to water in the condensates suggests that the gasoline yield was only about one-third of the potential due to the formation of the noncondensable hydrocarbons. This product slate is in general agreement with data reported by Mobil for the reaction conditions (15).

Primary Pyrolysis Vapors. After a catalyst regeneration cycle to remove residue from the methanol experiments, a slipstream of the primary pyrolysis vapors were passed over the ZSM-5 catalyst using steam as the carrier gas at a weight ratio of two parts of steam to one part of wood feed. The pyrolysis vapors were cooled from 510°C at the exit of the vortex reactor to 400°C at the entrance of the catalytic reactor. Figure 4 shows the temperature profile immediately prior to feeding the biomass, as well as 5-10 minutes later. The temperature profile with pyrolysis vapors as feed was not as large in magnitude as that seen with methanol and it had a very broad maximum. The heat of reaction of the pyrolysis vapors is less exothermic than for methanol and the steam carrier gas also has a moderating effect on the temperature rise. The broadness of the temperature profile reflects that the pyrolysis vapors are a complex mixture of compounds, which are probably reacting at different rates. The broader and lower temperature profile would make temperature control easier in a biomass-to-gasoline (BTG) reactor than in a methanol-to-gasoline (MTG) reactor. The location of the temperature maximum was monitored during the run, as shown in Figure 5. During the fairly short experiment, the temperature maximum was observed to move to the end of the reactor, indicating a fairly rapid deactivation of the catalyst had occurred. During this time, the composition of the hydrocarbon products appeared to be relatively constant. The GC chromatogram of the liquid hydrocarbons is shown in Figure 2b for comparison to the products made from methanol. As can be seen by inspection of the two gas chromatograms, the gasoline fraction (eluting before naphthalene) made from wood is very similar to that made from methanol. The composition of the gas formed over the catalyst from the pyrolysis vapors is shown in Table 3, as calculated from tracer gas concentrations before and after the reactor, along with the gas composition formed by the thermal decomposition of the pyrolysis vapors as determined previously (16); the catalytically formed gases had significantly less hydrogen and methane, but more carbon dioxide and propylene than the thermally formed gases. In comparing the composition of the gases formed by the catalytic conversion of the pyrolysis vapors to the catalytic conversion of the methanol, the relative hydrogen richness of the methanol becomes apparent in the relatively high hydrogen, methane, propane, and isobutane yields. The relative hydrogen richness is summarized by the empirical formulas for the two gas streams, in which the hydrogen-to-carbon ratio for the wood-derived gases is one-fourth that for the methanol-derived gases. This excessive amount of hydrogen in the methanol-derived gases suggests that methanol could be used as a hydrogen donor to hydrogen-poor feedstocks and this has been explored by several researchers (7, 10-12). The very low yield of isobutane from pyrolysis vapors would preclude the use of alkylation to incorporate the ethylene, propylene, and butenes into the gasoline product with a standalone process. Adsorption of the gaseous olefins onto cold ZSM-5 at low pressures may be a viable method to recycle them into the catalytic reactor. A comparison of Tables 2 and 3 reveals that the empirical gas composition calculated to have been made catalytically from the pyrolysis vapors corresponds to reaction (3), which has a thermal efficiency of 57%. However, the laydown of coke on the catalyst would serve to compete for the pyrolysis vapor feedstock and reduce the gasoline yields by reaction (5) as previously discussed. The quantitation of the coke is in progress.

DISCUSSION

Pyrolysis vapors made by the fast pyrolysis of softwood are very reactive with ZSM-5 catalyst to form a liquid hydrocarbon product, which is very similar to that formed from methanol. Although the catalyst is deactivated relatively quickly with pyrolysis vapors compared to methanol, other experimentation we have performed indicates that the catalyst can be oxidatively regenerated. This suggests that a catalytic reactor, which can maintain a high level of catalytic activity in spite of high coking rates, would be desired. This problem has been addressed and resolved by the petroleum refining industry which utilizes an entrained-bed reactor (riser-cracker), to crack heavy hydrocarbons to gasoline and about 5% to 15% coke, coupled with a fluidized-bed oxidative regenerator for the relatively slow, controlled oxidative coke combustion and catalyst regeneration (17). For the conversion of biomass to gasoline, these preliminary data are quite encouraging that a nearly direct conversion of biomass to gasoline can be accomplished at atmospheric pressures in one very rapid thermal cycle without the cost of hydrogen manufacture. With the calculated thermal efficiencies, it appears that there will be sufficient energy in the by-products to operate the process, even including the drying of a rather wet biomass feedstock prior to pyrolysis.

The gasoline product is almost entirely methylated benzenes with only a small amount of benzene. This gasoline would be expected to have octane ratings in excess of 100 and to have blending octane numbers between 115 and 135 based on reported blending octane values for the various methylated benzenes (18). Due to the expected continued demand for unleaded gasoline having higher octane numbers, the gasoline made from biomass by this process would be expected to command premium prices if sold to a petroleum refinery for blending purposes. The naphthalenic fraction of the organic products could easily be hydrocracked to increase the gasoline yields in a modern refinery (19). At this time, the phenolic by-products appear to be present in minor amounts and probably will not warrant recovery.

SUMMARY

The conversion of primary pyrolysis vapors made from biomass is a relatively new research and development area which is showing early promise. The extent to which the product slate can be manipulated by process variables will impact heavily on the viability of this process.

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Table 1. Reported Distribution of Oxygen in Inorganic By-Products with Various Feedstocks over ZSM-5 Catalyst

Compound	Oxygen Radical in Reactant*	% of Oxygen in By-Products			Reference
		H ₂ O	CO	CO ₂	
methanol	H, M	100	--	--	(8)
dimethyl ether	E, M	100	--	--	(8)
guaiacol	H, M	96	3	1	(10)
glycerol	H	92	7.5	0.5	(9)
xyleneol	H	93	6	1	(10)
eugenol	H, M	89	9	2	(10)
anisole	M	88	12	tr	(10)
2,4 dimethyl phenol	H	87	12	1	(10)
o-cresol	H	80	17	3	(10)
starch	H, E	78	20	2	(7)
isoeugenol	H, M	77	19	4	(10)
glucose	Cl, H, E	75	20	5	(6)
dimethoxymethane	M, E	73	6	21	(8)
xylose	Cl, H, E	60	35	5	(6)
sucrose	H, E	56	36	8	(6)
n-butyl formate	C2	54	46	0	(8)
diphenyl ether	E	46	46	8	(10)
furfural	Cl, E	14-22	75-84	2.5-3.0	(6, 9)
methyl acetate	C2	54	10	36	(11)
acetic acid	C2	50	4	46	(11)

*H = hydroxy; M = methoxy; E = C-O-C; Cl = carbonyl; C2 = carboxy

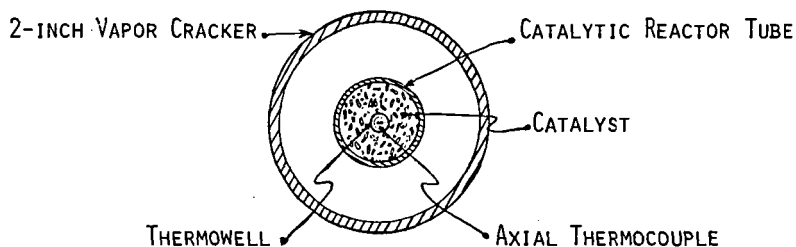


FIGURE 1. CROSS SECTIONAL VIEW OF THE FIXED-BED CATALYTIC REACTOR.

Table 2. Stoichiometric Relationships of By-Products to Gasoline Yields using Primary Softwood Pyrolysis Vapors as the Feedstock

	Assumed Reaction	U.S. Gal Gasoline*		Wt Gasoline*		Energy in Gasoline*	
		Ton Dry Wood		Wt Wood		Energy in Wood	
1)	$\text{CH}_{1.2}\text{O}_{0.49} + 0.100 \text{ C}_8\text{H}_{10} + 0.20 \text{ CO}_2 + 0.10 \text{ H}_2\text{O}$	99		0.35		0.75	
2)	$\text{CH}_{1.2}\text{O}_{0.49} + 0.085 \text{ C}_8\text{H}_{10} + 0.32 \text{ CO} + 0.23 \text{ H}_2\text{O}$	84		0.30		0.64	
3)	$\text{CH}_{1.2}\text{O}_{0.49} + 0.073 \text{ C}_8\text{H}_{10} + 0.42 \text{ CH}_{0.65}\text{O}_{0.82} + 0.10 \text{ H}_2\text{O}$	75		0.27		0.57	
4)	$\text{CH}_{1.2}\text{O}_{0.49} + 0.022 \text{ C}_8\text{H}_{10} + 0.824 \text{ C} + 0.49 \text{ H}_2\text{O}$	22		0.08		0.17	
5)	$\text{CH}_{1.2}\text{O}_{0.49} + \text{CH}_{0.22} + 0.49 \text{ H}_2\text{O}$ ("coke")	0		0		0	

*Yields reflect an assumed 70 wt % conversion of softwood to primary pyrolysis vapors.

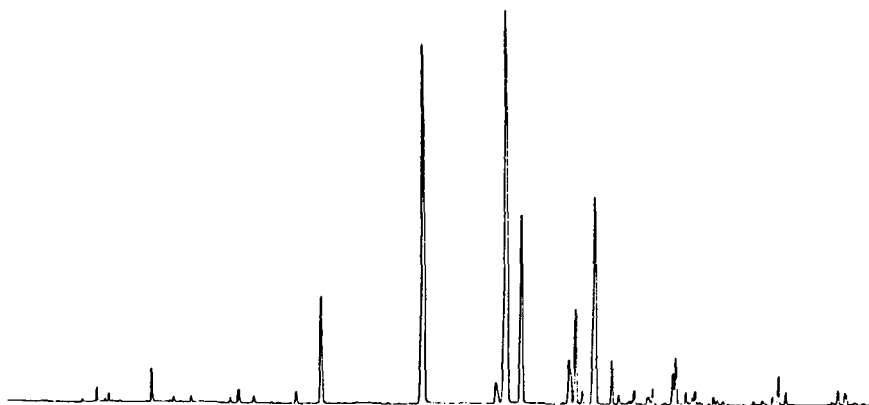


FIGURE 2A. GC OF HYDROCARBON PRODUCTS MADE FROM METHANOL AT 400°C WITH ZSM-5 CATALYST

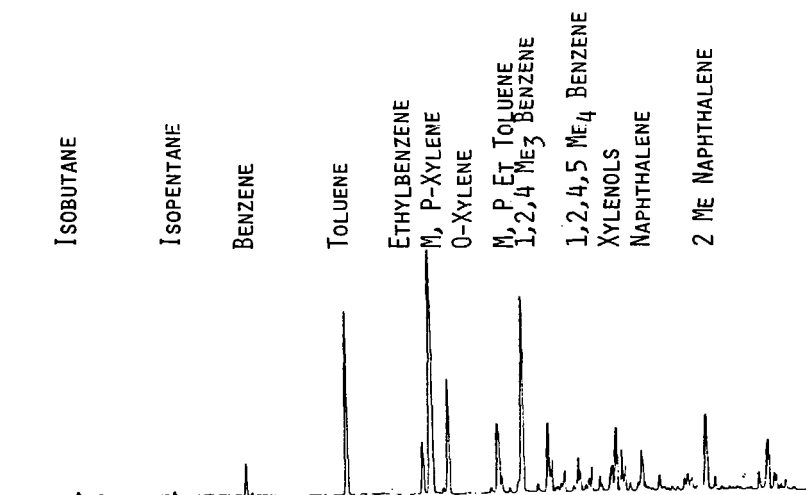


FIGURE 2B. GC OF HYDROCARBON PRODUCTS MADE FROM SOFTWOOD PRIMARY PYROLYSIS OIL VAPORS AT 400°C WITH ZSM-5 CATALYST

Table 3. Calculated Molar Compositions of Net Product Gases
(ZSM-5 containing catalyst - Mobil's MCSG-2)

Feed Reactor	Softwood Pyrolysis Vapor ($\text{CH}_{1.2}\text{O}_{0.49}$)		(CH ₄ O) Methanol	
	Thermal (Run 55)	Catalytic (Run 76-C)	Thermal (Run 74-C)*	Catalytic (Run 75-C)
H ₂	10.6	-0.6	62.8	18.4
CO	59.4	69.8	31.1	4.4
CO ₂	5.6	15.2	1.4	2.8
CH ₄	12.2	1.4	2.1	16.2
C ₂ H ₂	0.5	—	—	—
C ₂ H ₄	5.3	5.0	1.6	5.3
C ₂ H ₆	1.1	0.3	0.3	4.1
C ₃ H ₆	1.9	6.0	0.7	5.3
C ₃ H ₈	—	0.5	0.4	17.8
C ₄ H ₈	1.1	1.2	—	2.3
iso-C ₄ H ₁₀	—	0.2	0.1	14.4
n-C ₄ H ₁₀	—	—	—	5.3
C ₅ ⁺	2.4	—	—	3.6
Empirical Formula	CH _{1.3} O _{0.65}	CH _{0.65} O _{0.82}	CH _{3.6} O _{0.8}	CH _{2.7} O _{0.05}

*In this run, the methanol is thought to have thermally decomposed for the most part prior to reaching the catalyst.

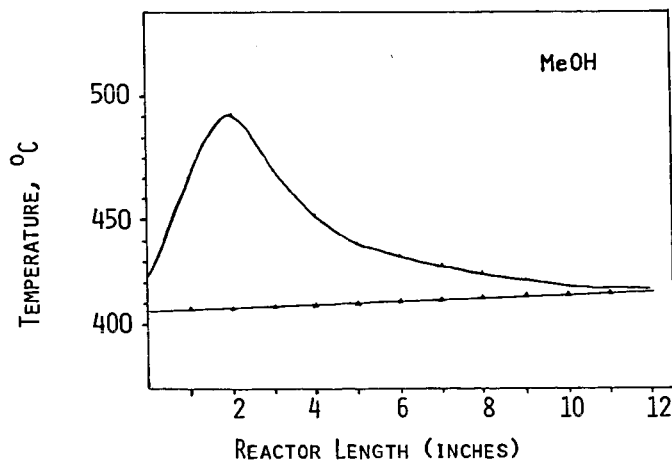


FIGURE 3. TEMPERATURE PROFILE FOR METHANOL REACTANT

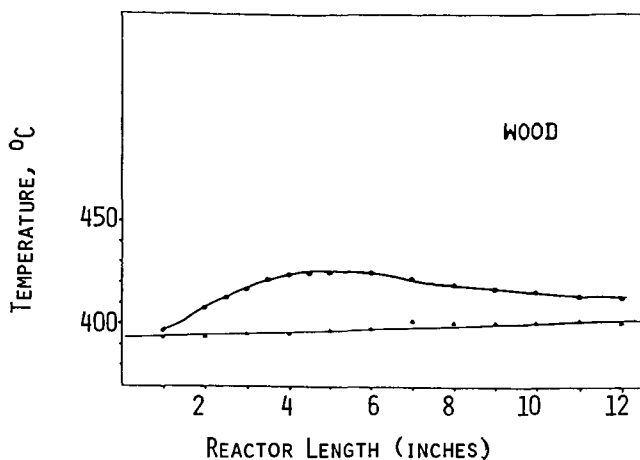


FIGURE 4. TEMPERATURE PROFILE FOR SOFTWOOD PYROLYSIS VAPORS AS THE REACTANTS

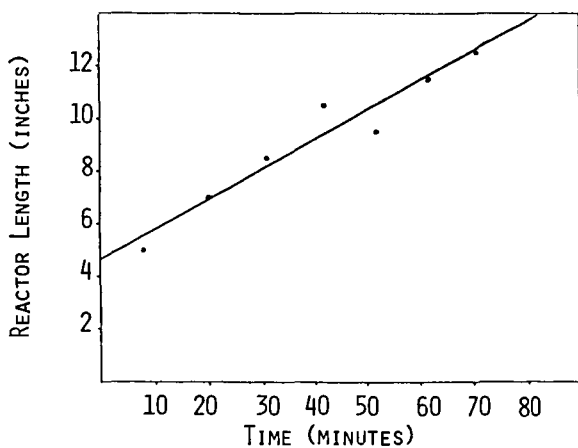


FIGURE 5. LOCATION OF THE MAXIMUM CATALYST BED TEMPERATURE, SHOWING CATALYST DEACTIVATION

REACTIONS OF BIOMASS PYROLYSIS OILS OVER ZSM-5 ZEOLITE CATALYSTS

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INTRODUCTION

It has been shown that synthetic zeolites such as ZSM-5 can be used to convert oxygenated compounds derived from biomass materials into hydrocarbon compounds which can be used as fuels and chemical feedstocks (1,2,3,4).

However, the pyrolysis oils obtained from woods by different thermoliquefaction processes (5,6), show poor hydrocarbon yield and high tar content when contacted over ZSM-5 zeolite catalysts at high temperature (7,8). Since the pyrolysis oils are composed of a wide variety of oxygenated compounds such as cyclopentanone, furfural, phenol, acid and carbohydrate derivatives (9,10), it is difficult to point out exactly which family of compounds is contributing more to the observed tar content and to the deactivation of the catalysts. Catalytic studies on model compounds which are generally found in the pyrolysis oils are therefore primordial in order to determine the best catalytic system. The reactions of phenolic compounds over ZSM-5 catalysts are already reported (8). The present paper thus reports the results for the conversion of cyclopentanone, furfural, glucose and its isopropylidene derivative over H-ZSM-5, Zn-ZSM-5 and Mn-ZSM-5 zeolite catalysts at temperatures ranging from 400°C to 500°C. Some reactions are supplemented with methanol in their feeds so as to determine the effect of increased hydrogen to carbon effective ratio on the deoxygenated hydrocarbon yields.

EXPERIMENTAL

Preparation and characterization of catalysts

The ammonium form of ZSM-5 was prepared according to a published procedure (11). The H-form of the catalyst was obtained by calcination at 500°C for 10 hours. The zinc and manganese loaded catalysts were prepared by ion exchange in a 10% aqueous solution of $\text{Zn}(\text{NO}_3)_2$ and $\text{Mn}(\text{NO}_3)_2$ at ~ 80°C. After washing and drying at 160°C over night, the solid was calcined for 10 hours at 520°C. The X-ray diffraction pattern of the three synthetic ZSM-5 are similar to those reported in the literature. The chemical composition of ZSM-5 samples are shown in table 1.

Apparatus

The catalytic conversion were studied in a continuous flow quartz reactor with a fixed bed of diluted catalysts. The reaction conditions are reported in table 1. After an experimental run (about 3 hours), the tar on the catalytic bed was determined by taking the difference in weight of the reactor before and after placing it in a furnace set at 500°C on the presence of air. The reaction products were analyzed by GC and GC/MS (table 1).

RESULTS AND DISCUSSION

Figure 1 shows the yield of conversion, $\text{C}_1 - \text{C}_6$ aliphatics, aromatics, polyaromatics and tar as a function of reactor temperature for pure cyclopentanone over H-ZSM-5/bentonite (80/20) catalyst. The conversion is completed at 350°C. The

main reaction is thermal decarbonylation giving C_4 hydrocarbons that react further on the catalytic bed to produce aliphatic aromatic and polyaromatic hydrocarbons.

Table 2 shows the reaction of pure furfural ($(H/C)_{eff} = 0$) over various cation exchanged ZSM-5 catalysts at $400^\circ C$. The deoxygenated hydrocarbon yields range from 6.6 to 9.4% and the oxygenated hydrocarbon yields range from 25.6 to 50.0%. These values reflect the poor performance of all three catalysts in deoxygenating furfural. The large quantities of furan and CO observed is due to thermal decarboxylation of furfural. Higher tar contents were observed for the metal exchanged catalysts (21.2 and 25.9%) than the hydrogen exchanged catalyst (14.2%). The low water contents (range of 2.7 to 7.0) produced from these reactions indicate poor catalytic deoxygenation of furfural. CO_2 , which is produced from pyrolytic reactions, is obtained in low yields. The yields for the aliphatics ($9.0 \pm 1.4\%$) and olefins ($8.5 \pm 2.1\%$) are comparatively smaller than those for the aromatics ($47.7 \pm 3.5\%$) and polyaromatics ($34.7 \pm 3.8\%$). Polyaromatics are usually produced on the surface of the zeolite because they are too large to enter or leave the channels of the zeolite; high values for these compounds are undesirable because they are not usefull as chemical feedstocks.

Figure 2 shows the product distributions for the reaction of various furfural/methanol mixtures over H-ZSM-5/bentonite (80/20) at a reactor temperature of $450^\circ C$; only the major components in the products are shown. The abscissa in figure 2 is given in both increasing percentage of methanol and increasing $(H/C)_{eff}$ for the feed. As methanol increases the yields for deoxygenated hydrocarbons and water increase while those for tar, furan and CO decrease. The drastic increase of deoxygenated compounds and water and decrease of furan with increasing methanol concentration indicate that significant catalytic deoxygenation is taking place. At about 55% methanol/45% furfural ($(H/C)_{eff}$ of 0.85, there is complete removal of furan from the reaction products; only small quantities of other oxygenated hydrocarbons were present ($< 0.26\%$). The yields for the other products were similar to those observed previously for furfural. Only at 70% methanol/30% furfural there was a significant reduction in the tar content, i.e. 6.7% (14.1% on carbon basis). The average CO_2 present was $0.3 \pm 0.1\%$.

Table 3 shows the product distribution for reactions of furfural/methanol (30/70) over various concentrations of H-ZSM-5 at $450^\circ C$. By diluting the catalyst with bentonite from 80 to 18%, the deoxygenated hydrocarbon yield increased from 30.6 to 41.4%. Changing the support material from bentonite to Al_2O_3/SiO_2 caused a small reduction in the deoxygenated hydrocarbon yield (36.3%); there was, however, less coke formed when compared to the other two cases. The product selectivities were similar to those of previous cases.

Table 4 shows results for reactions of glucose and glucose derivative done over 80% H-ZSM-5 and 20% bentonite at $450^\circ C$. With an increased $(H/C)_{eff}$, there were increased deoxygenated hydrocarbon yields for the glucose/methanol/water (20.0/30.0/50.0) and glucose derivative/methanol/water (27.6/60.2/12.2) cases when compared to that of the glucose/water (20.3/79.7) case. Also, there was a simultaneous decrease in tar content with an increase in $(H/C)_{eff}$. However, in all cases the hydrocarbon yields are poor and the tar contents are too high. The high water content observed in all experiments (29.2 to 66.1%) is not only due to catalytic deoxygenation through loss of water but also due to polycondensation reactions of glucose and its derivative. These condensation reactions produce polymeric oxygenated compounds which are responsible for the high tar content observed. Oxygenated hydrocarbons, CO and CO_2 , are minor products which are normally obtained from thermal decomposition of biomass materials (12). The product selectivity indicates a high percentage of aliphatics (23.6 to 50.5%) and aromatics (34.2 to 53.2%).

Except for the reaction with glucose/water, the olefin contents are low for the other two reactions. The production of polyaromatics (mainly indene and naphthalene derivatives) is rather high (2.56 and 7.24%) considering that they are produced from the surface of the zeolite rather than in the channels of the zeolite.

To test the efficiency of the catalyst, experiments were done with 18% H-ZSM-5 (instead of 80%) dispersed in 82% bentonite. Also, the catalytic bed would have less acidic sites (Brönsted sites) which are known to promote polymerization of the carbohydrates and hence reduce the deoxygenated hydrocarbon yield. Table 5 shows the results for experiments done on the diluted catalytic bed. Only in the glucose/methanol/water (20.0/30.0/50.0) case there was a significant increase in the deoxygenated hydrocarbon yield and a decrease in tar content. Hence, reducing the number acidic sites does not reduce the extent of the polymerization of the carbohydrates. However, there was an increase in the polyaromatic content in table 5 compared to that in table 4 indicating that there is more surface reaction in the dilute catalyst case.

When the catalytic support material was changed from bentonite to a mixture of Al_2O_3 and SiO_2 , the yield of deoxygenated hydrocarbon increased for both cases as showed in table 6 when compared for similar cases in tables 4 and 5. There were also a comparable decrease in tar content for these reactions.

Deoxygenation of glucose/water (20.3/79.7) with manganese and zinc exchanged ZSM-5 are reported in table 7. There are a reduction in the deoxygenated hydrocarbon yields when compared to similar reactions in tables 4 and 5. The tar contents were just as high as the reactions before. The product selectivity which is normally influenced by these metal exchanged zeolites were not very different from those reported before.

CONCLUSION

Cyclopentanone is deoxygenated with high yield to hydrocarbons over H-ZSM-5 at 400°C. The reaction of furfural over ZSM-5 catalysts at 400°C and higher temperatures produce pyrolytic products which are volatile and non-volatile. The volatile fraction are deoxygenated to produce hydrocarbon products while the non-volatile fraction remain on the catalytic bed causing desactivation of the zeolite and enhancement of the tar content. Glucose and its isopropylidene derivative undergo thermal reactions which produce a significant amount of tar and a small amount of volatile products. The volatile fraction are deoxygenated by ZSM-5 catalysts to produce hydrocarbon products.

ACKNOWLEDGEMENT

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TABLE 1
Chemical composition of ZSM-5 samples

Component (WT%)	H-ZSM-5	Mn-ZSM-5	Zn-ZSM-5
Na ₂ O	0.55	0.69	0.49
Al ₂ O ₃	2.25	2.33	2.10
SiO ₂	86.86	91.05	87.62
MnO ₂	---	0.78	---
ZnO	---	---	0.26
TiO ₂	0.59	0.64	0.38
L.O.I.*	7.62	3.26	6.68
<u>Molar Ratio</u>			
SiO ₂ /Al ₂ O ₃	65.47	66.32	70.80
Na ₂ O/Al ₂ O ₃	0.40	0.49	0.38

* L.O.I. means loss on ignition of sample weight.

REACTION CONDITIONS

Catalyst weight : 10 g (80% ZSM-5 + 20% bentonite)
 Temperature : 350-560°C
 Pressure : atmospheric pressure
 Inert gas : helium (~ 3 ml/min)
 WHSV ** : variable
 Reaction time : 3 hours

** The weight hourly space velocity (WHSV) is defined as:

$$\text{WHSV} = \frac{\text{g of injected feed per hour}}{\text{g of catalyst}}$$

ANALYTICAL CONDITIONS

- Gas chromatography : HP 5890 GC with DB-5 (SE-54)
column (30 m x 0.25 mm, 1.0 μ)
- For liquid : 70°C (4 min), then 4°C/min to 160°C
then 20 min at 160°C
- Gas : 33°C (isothermal)
- GC/MS : HP 5890 GC and MS detector
Pona column and DB-5 column

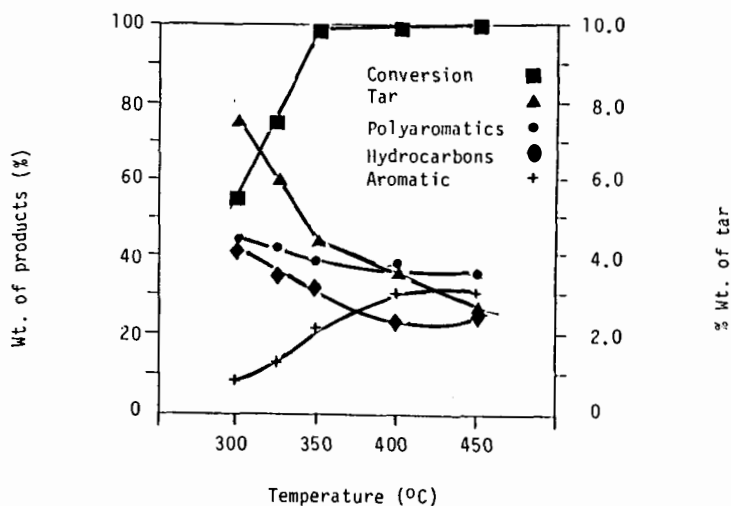


Figure 1: Reaction of cyclopentanone over H-ZSM-5/bentonite (80/20) at different reactor temperature

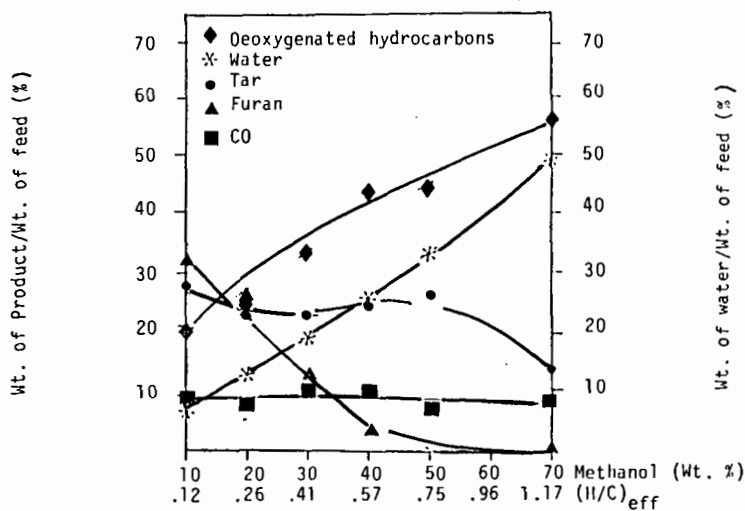


Figure 2: Reaction of furfural/methanol mixtures over H-ZSM-5/bentonite (80/20) at a reactor temperature of 400°C and a WHSV of $0.238 \pm 0.018 \text{ hr}^{-1}$.

TABLE 2

Reaction of furfural over cation exchanges ZSM-5 at 400°C and WHSV of 0.281 hr⁻¹

Experimental conditions:

Catalyst composition:	80% H-ZSM-5 20% bentonite	80% Zn-ZSM-5 20% bentonite	80% Mn-ZSM-5 20% bentonite
Total product distribution (WT%)			
Furan	47.0	23.8	27.8
Oxygenated hydrocarbons	50.0	25.6	40.7
Tar	14.2	21.2	25.9
CO	22.8	36.3	17.9
CO ₂	0.56	4.84	1.89
H ₂ O	4.39	2.69	6.97
Deoxygenated hydrocarbons	8.00	9.42	6.64
Product selectivity (WT%)			
Aliphatics, C ₁ - C ₈	8.84	7.62	10.5
Olefins, C ₂ - C ₆	8.46	10.6	6.48
Aromatics	50.6	48.8	43.9
Polyaromatics	32.1	32.9	39.1

TABLE 3

Reaction of furfural/methanol (30/70) feed ((H/C)_{eff} of 1.17) over H-ZSM-5 at 450°C

Experimental conditions:

Catalyst composition:	80% H-ZSM-5 20% bentonite	18% H-ZSM-5 82% bentonite	18% H-ZSM-5 48% Al ₂ O ₃ 34% SiO ₂ 1.26
WHSV (Hr ⁻¹)	0.029	1.26	
Total product distribution (WT%)			
Oxygenated hydrocarbons*	---	1.36	0.83
Tar	6.74	7.60	4.90
CO	9.44	7.84	7.25
CO ₂	0.48	0.58	0.30
H ₂ O	52.7	41.6	50.4
Deoxygenated hydrocarbons	30.6	41.1	36.3
Product selectivity (WT%)			
Aliphatics, C ₁ - C ₈	1.82	11.6	20.7
Olefins, C ₂ - C ₆	2.90	3.01	3.63
Aromatics	83.5	72.8	60.8
Polyaromatics	11.9	12.6	14.8

* Mainly furan and benzofuran, derivatives and dimethylether.

TABLE 4

Reaction of glucose and glucose derivative over 80% H-ZSM-5
and 20% bentonite at 450°C

Experimental conditions:

Reactant composition:	20.3 glucose 79.7% water	20.0 glucose 30.0% methanol 50.0% water	27.6 glucose derivative 60.2% methanol 12.2% water
WHSV (Hr ⁻¹)	0.062	0.195	0.313
(H/C) _{eff}	0.0	1.59	1.36
Total product distribution (WT%)			
Oxygenated hydrocarbons	---	0.70*	3.87**
Tar	65.1	33.3	14.1
CO	2.14	0.46	0.23
CO ₂	1.48	1.41	0.92
H ₂ O	29.1	59.7	66.1
Deoxygenated hydrocarbons	2.18	4.43	14.8
Product selectivity (WT%)			
Aliphatics, C ₁ - C ₈	23.6	35.7	50.5
Olefins, C ₂ - C ₆	41.6	3.81	2.74
Aromatics	34.8	53.3	43.2
Polyaromatics***	---	7.24	3.56

TABLE 5

Reaction of glucose and glucose derivative over 18% H-ZSM-5
and 82% bentonite at 450°C

Experimental conditions:

Reactant composition:	20.3% glucose 79.7% water	20.0% glucose 30.0% methanol 50.0% water	27.6% glucose derivative 60.2% methanol 12.2% water
WHSV (Hr ⁻¹)	0.862	1.195	1.12
(H/C) _{eff}	0.0	1.59	1.46
Total product distribution (WT%)			
Oxygenated hydrocarbons	0.58*	0.96*	4.20**
Tar	51.3	21.0	11.1
CO	3.79	1.76	0.84
CO ₂	2.82	0.29	0.79
H ₂ O	39.4	57.9	64.3
Deoxygenated hydrocarbons	2.15	18.1	18.8
Product selectivity (WT%)			
Aliphatics, C ₁ - C ₈	29.0	43.6	17.5
Olefins, C ₂ - C ₆	7.33	1.18	14.0
Aromatics	45.2	45.3	55.8
Polyaromatics***	18.3	9.99	12.7

* Mainly furan and benzofuran derivatives; ** Mainly acetone and furan derivatives; *** Mainly indene and naphthalene derivatives

TABLE 6

Reaction of glucose and glucose derivative over 18% H-ZSM-5
and 48% Al_2O_3 and 34% SiO_2

Experimental conditions:

Reactant composition:	20.0 glucose 30.0% methanol 50.0% water	27.6 glucose derivative 60.2% methanol 12.2% water
WHSV (Hr^{-1})	1.18	1.11
$(H/C)_{eff}$	1.59	1.46
<u>Total product distribution (WT%)</u>		
Oxygenated hydrocarbons	0.12	0.24
Tar	14.3	6.86
CO	1.59	1.76
CO ₂	0.44	0.47
H ₂ O	62.4	53.5
Deoxygenated hydrocarbons	21.2	37.2
<u>Product selectivity (WT%)</u>		
Aliphatics, C ₁ - C ₈	19.0	21.0
Olefins, C ₂ - C ₆	12.0	8.32
Aromatics	65.6	62.0
Polyaromatics	3.42	8.66

TABLE 7

Reaction of 20.3% glucose and 79.7% water over manganese
and zinc exchanged ZSM-5

Experimental conditions:

Catalysis composition	80% Mn-ZSM-5 20% bentonite	80% Zn-ZSM-5 20% bentonite
WHSV (Hr^{-1})	0.046	0.055
$(H/C)_{eff}$	0.0	0.0
<u>Total product distribution (WT%)</u>		
Oxygenated hydrocarbons	---	---
Tar	72.3	53.1
CO	2.60	2.23
CO ₂	1.91	4.19
H ₂ O	22.3	39.8
Deoxygenated hydrocarbons	0.89	0.68
<u>Product selectivity (WT%)</u>		
Aliphatics, C ₁ - C ₈	26.0	35.4
Olefins, C ₂ - C ₆	42.8	2.60
Aromatics	31.0	62.0
Polyaromatics	---	---